

Modern Chlor-Alkali Technology

Volume 8

EDITED BY

John Moorhouse
Rhodia Ltd
Hollingwood
Chesterfield
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UK

Proceedings of the 2000 London
International Chlorine Symposium
Organised by SCI's Electrochemical Technology Group,
held on 31st May–2nd June, 2000

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Modern Chlor-Alkali Technology
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Introduction

The chapters in this volume were presented as papers at the 2000 London International Chlorine Symposium held at the Millennium Conference Centre, Gloucester Hotel from 31st May to 2nd June 2000. This was the ninth in the series organised by the Electrochemical Technology Group of the Society of Chemical Industry.

The symposium, again, attracted strong support. Of the papers submitted, 26 were selected for presentation to address the latest technological, economic, political, environmental and safety developments facing the industry today.

The programme included:

- (1) A view on the future of the business.
- (2) The issues of mercury cell phase out and risk assessment of chlorine compounds.
- (3) Developments in electrodes and electrode coatings.
- (4) Developments in cell design and operation for all three technologies.
- (5) Conversion studies and experiences.
- (6) Developments in chlorine processing technology and effects on economics.

The event was attended by 202 delegates from 29 countries.

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John S Moorhouse
Chairman – Organising Committee
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Chapter 1

The Chlor-Alkali Business

D J Hutchison

1.1 Introduction

This chapter examines the business of the chlor-alkali industry. Without a need for chlorine there is no chlor-alkali business. This industry is now in its second century and having passed the millennium bug without any serious interruption, the future can now be examined. In this chapter there is an emphasis on chlorine rather than alkali as the alkali industry is thousands of years old and has been documented extensively since the time of the ancient Egyptians.

The chlorine industry really took off at the end of the 1890s with the installation of the first mercury cell units. Since then the industry has coped with many problems, the main one being the fixed amount of caustic soda per ton of chlorine out of the cells. There have always been imbalances on the demand for chlorine and the demand for caustic soda. The two products quite often go their own way and no reason is seen to change this situation.

What has happened over the years has been an increasing trend in the industry to globalise. This means that the effect on a market at the other end of the world can have an impact on a domestic market. There are several reasons for this: improved communications, multinational purchasing of caustic, more transparency, and, according to one producer, too many consultants.

There have been many pressures on the industry in addition to the need to make a profit. Legislation on the production of chlorine, the technology of choice, the use of chlorine in some applications as well as the destiny of some derivatives have all added to the burden of managing the business. Many great names from the past century have already disappeared or will disappear soon as far as chlorine production is concerned. Several companies have decided to exit the chlorine chain altogether in a move to convert either to specialities or life sciences. This has added to the problems of managing what is in normal times a dynamic business. Constant managerial problems such as downsizing, spinning off and merging can cause the eye to miss the ball or worse miss the big picture altogether. Today there is the possibility of buying and selling caustic soda on the Internet.

The opening chapter of this book looks at current issues in the chlor-alkali business and attempts to look at the issues which lie ahead.

1.2 Chlor-alkali production issues

Chlor-alkali production has been rising steadily over the last few years although the Asian crisis resulted in a global slow-down (see Table 1.1). Demand for chlorine has again been rising; however, this rise in demand was not followed immediately in the market for caustic soda. In early 2000 the market for chlorine appeared to be the stronger of the two though price rises were sought in the USA for both products.

Table 1.1 World chlorine supply/demand (per year $\times 10^3$ tons). Source: Tecnon (UK) Ltd.

Year	1995	1997	1999	2001	2003	2005
Production capacity	46.0	48.7	51.3	52.9	54.5	54.7
Production	38.0	39.5	40.3	42.0	44.5	46.4
Capacity utilisation	82.6	81.1	78.5	79.4	81.7	84.8
Consumption in non-vinyl	26.0	26.0	25.8	26.8	27.9	28.5
Chlorine contained in PVC	12.4	14.5	15.7	16.5	18.1	19.6
Chlorine recovered from HCl	(0.4)	(1.0)	(1.2)	(1.3)	(1.5)	(1.7)
Net chlorine demand	38.0	39.5	40.3	42.0	44.5	46.4
Annual growth						

The returns for the industry can be monitored (see Figs 1.1–1.3). The selling price of caustic soda is fairly transparent everywhere and chlorine pricing is transparent in the USA. Chlorine is less transparent outside the USA as most of the consumption is captive rather than merchant. The market for ethylene dichloride (EDC) is, however, transparent and chlorine values can be worked out from the selling price of the EDC and the input price for the ethylene. Knowledge of the chlorine value and the caustic value gives the value of the Electrochemical Unit or ECU. This provides a measure of the profitability of the business at any time. Convenient marker prices can be found in the US Gulf for both EDC and caustic as well as out of north-west Europe.

From several price histories it is possible to establish caustic soda and chlorine values in different markets and hence calculate the ECU value and with it some measure of profitability. The chlorine value in export EDC can be calculated on the formula assuming the ethylene price is known. The chlorine value using hydrogen chloride is complicated by the extra costs of using HCl rather than chlorine and the slightly lower yields with oxychlorination, though that too can be calculated to give a chlorine value.

The industry has to face technology changes. The advent of membrane cells can

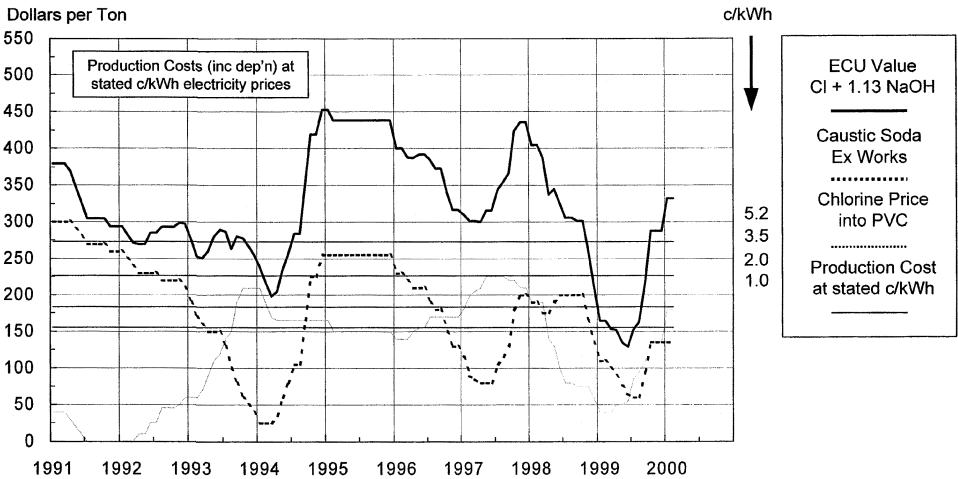


Fig. 1.1 Value of ECU in the United States. Source: Tecnon/Anorganica. Production cost at stated DM/kWh (—).

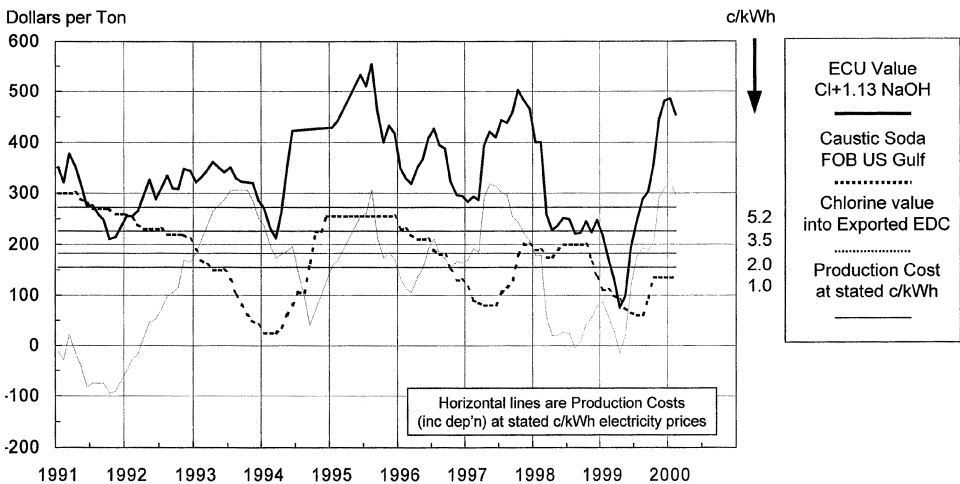


Fig. 1.2 Value of ECU in the United States from exported caustic, and from chlorine in exported EDC. Source: Tecnon/Anorganica. Production cost at stated DM/kWh (—).

allow for an alternative to mercury cell production as well as asbestos diaphragm production. There is pressure on both methods of production and while the solutions are there, in some cases no economic reason can be found for an earlier than expected shutdown of a cell room. The energy savings in Europe would not in themselves justify a conversion of the six million tons of capacity.

If mercury shutdowns were to occur without replacement then Europe would be forced into importing chlorine derivatives such as EDC to compensate. The future of asbestos in diaphragm cells is also an issue, but with a much lower profile in Europe this has attracted less attention apart from in France. In the USA there are pressures on the industry too, which could be more acute depending on who occupies the White

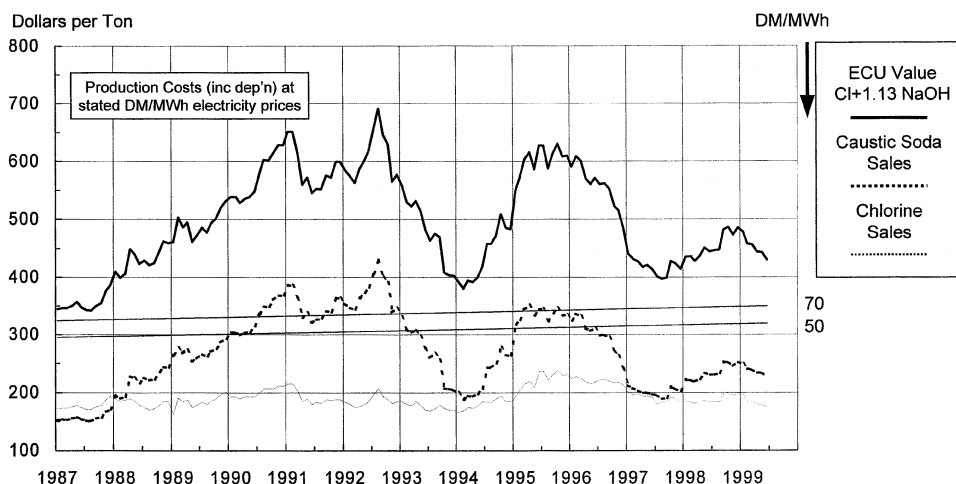


Fig. 1.3 Value of ECU in Western Europe for domestic sales. Data source: Statistisches Bundesamt/Tecnion. Production cost at stated DM/kWh (—).

House after the departure of the Clinton administration. Elsewhere the build-up of capacity in membrane caustic has picked up speed, especially in Asia where there was a slight delay owing to the crisis.

In looking to the future, many chlor-alkali units have either their own in-house power source or a co-generation unit nearby with the avoidance of having to buy from a utility. Many chlor-alkali producers have become power generators in their own right and can control chlorine production by diverting power to the grid instead. An example of this was in 1999 during the very hot summer period in the USA with demand for power in air conditioning offering prices as high as 10 cents per unit compared with power costs of 2.6 cents normally found in the Gulf Coast states.

Energy costs should gradually be lowered for many chlorine producers. Less predictable are the interference of governments and the imposition of taxes in the guise of climate change. The UK government got very near to imposing such a tax, which would have shut down a considerable part of the industry.

The rise in capacity of EDC and caustic exporting units has implications for some high-cost integrated units especially in Europe where a decision will have to be taken on the future of the mercury cell units. Does it make sense to import EDC and use that in the vinyl chain or to continue to compete against a market fed by 'cheap' EDC out of the Middle East? The same would apply to Japan, though Japan has been importing considerable amounts of EDC for years (see Figs 1.4 and 1.5).

Looking further ahead, the commercialisation of the EVC process for the direct chlorination of ethane with its expected cost savings would challenge the cost structures of conventional plants leading to VCM capacity being built in very low-cost regions for both ethane and power. Obviously where the chlorine is made will

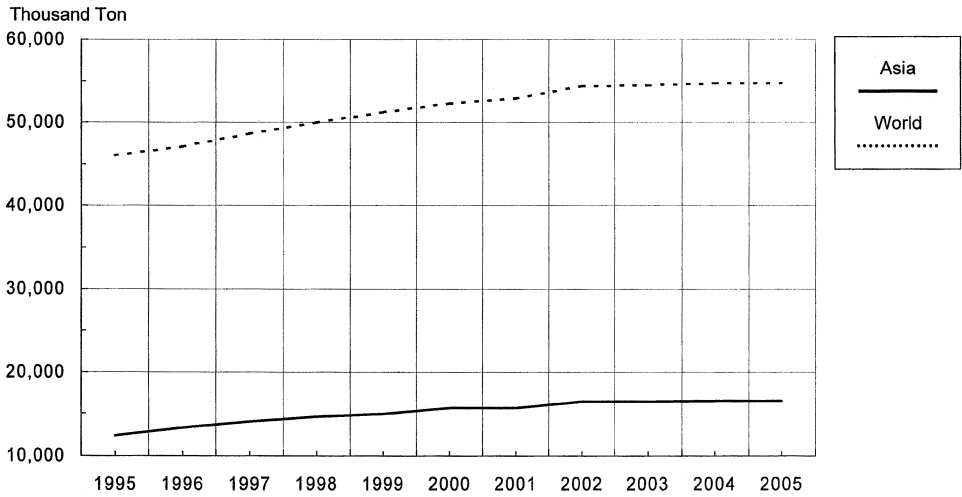


Fig. 1.4 Build-up of chlorine capacity in Asia and world total. Source: Tecnon/Anorganica.

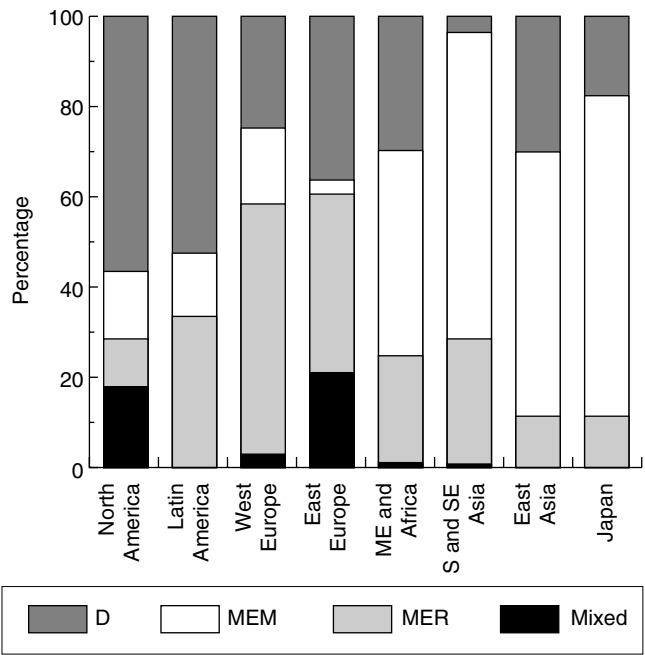


Fig. 1.5 Chlorine capacities: process profiles for 1999. Source: Tecnon/Anorganica.

dictate where the caustic is produced. EVC commissioned a pilot plant in Wilhelmshaven in Germany in May 1998 and trials have proceeded to prove the process under full industrial conditions. More research will be done to confirm a commercial process. EVC has said that the technology could reduce the cash costs of PVC by one-third as well as decoupling the vinyl chain from ethylene crackers.

1.3 Cost structure issues

Consolidation in the next century will result in cost savings from the economies of scale alone. The trend to focus chlor-alkali in low-energy-cost regions will continue. Energy savings will also likely be made in the cell technology.

The development of the membrane cell cut the energy consumption in chlor-alkali production. A good cell will produce a ton of caustic for around 2400 kWh. Membrane caustic can only be produced up to around 35%. Several cell designers have tried to develop a cell and membrane combination that would allow 50% caustic to be made, but this has proved to be commercially elusive so far. Membrane cells have probably reached the theoretical limit on energy consumption for a commercial plant. In Japan, power consumption has been cut by 30% over the last 20 years as the conversion from mercury cell progressed.

There will be a trend to large green-field sites using the bipolar membranes designed to work at high current densities, i.e. in excess of 6 kA m^{-2} . Looking even further ahead there are new methods of electrolysis being developed to cut down the energy consumption in producing the ECU. For example, MITI in Japan has been developing a gas diffusion electrode, which may cut the power consumption further by 30 or even 40%. This electrode would be used as the cathode in a cell system and there would be no production of hydrogen. The energy savings come from the lower theoretical electrolysis energy as well as the cancellation of the hydrogen overvoltage. The cell development has been taking place at various companies and cell life of two years is now expected with further research being done to extend the electrode life to five years. The Japan Soda Association has estimated the power consumption to be 1500 kWh per ton of caustic produced.

The progressive savings on the development of cell technology can be seen in the chart shown in Fig. 1.6. These savings are significant and may encourage rapid change from mercury cell in countries where the benefits of membrane have not yet been proved in terms of energy cost savings. If this technology is proved there will be great pressure on some countries to force this method through with the imposition of a carbon tax.

1.4 The balance

There are no grounds for believing that the chlorine and caustic soda balances will eventually become manageable. Consolidation in the company portfolio may result in the number of producers becoming much smaller and with that a degree of control will be gained, especially in the operating rates. With fewer producers chasing a 'market' share there may be some stability in controlling the downside in the cycle. Chlor-alkali producers lose heavily when operating rates are low and demand for caustic is sluggish. The ECU then generates very low returns as was seen last year in the USA.

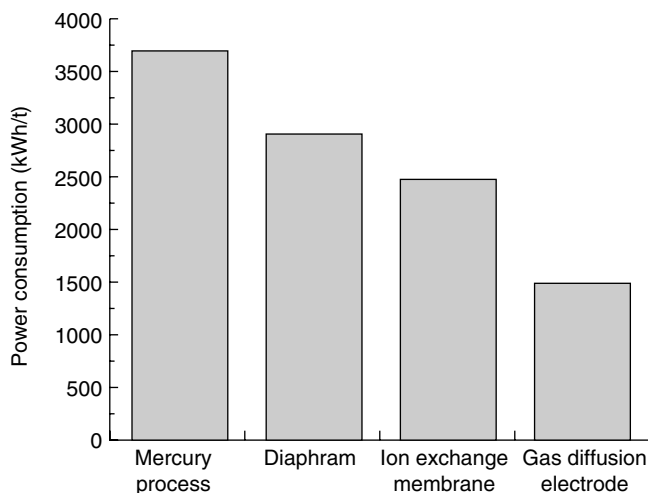


Fig. 1.6 Electric power consumption rate by each method.

Data source: Japan Soda Industry Association

Increased consumption of HCl in the vinyl chain has allowed for better chlorine management. For example, it is now quite common to tie in a VCM complex to an isocyanate unit. This has two effects. Firstly, the hydrochloric acid production is usefully consumed and obtains real chlorine values rather than the acid market values. Secondly, increased use of HCl cuts the need to build some chlorine capacity and hence cuts the amount of caustic soda produced and which has to be sold. The balance can therefore be 'adjusted' by the recycling of HCl in the system.

Nevertheless the age-old problem of balancing will not go away. Chlorine cannot be stored so if demand falls there has to be a rate cut eventually or wholesale conversion of EDC back to the 3 cent per pound level. At the other extreme, caustic soda cannot be put into inventory for ever. Caustic soda at the \$30 level implies high chlorine values, which implies better use of the chlorine, especially where HCl is a co-product. Again, looking into the future, more isocyanate and epichlorohydrin units will be tagged on to the vinyl chain as is projected for China and Qatar in the twenty-first century. This ought to minimise the amount of co-product caustic produced (see Fig. 1.7).

In the twenty-first century the mixture of politicians, bankers and, dare I say it, some consultants will have seen to it that we still have periods of 'boom and bust', in other words periods of strong growth and periods of recession. The demand for chlorine and caustic will not be the same and hence the imbalances are likely to be a fact of life though how they are controlled will be a function of the producers if there is some serious consolidation.

While the industry has to balance out globally there are none the less regional imbalances. Asia still has a deficit of chlorine derivative production and a large demand for PVC. Much of this is met with imported EDC as the feedstock. The EDC in normal times comes mainly from low-energy-cost regions such as the Middle East

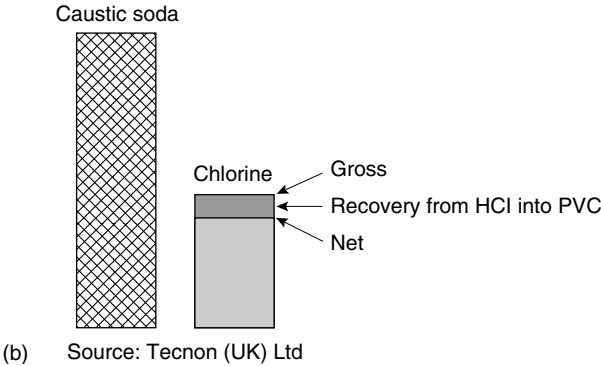
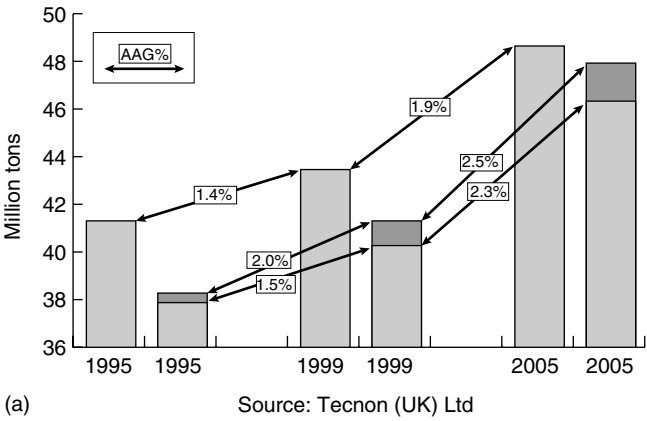


Fig. 1.7 (a) World chlorine versus caustic soda consumption. AAG = average annual growth. (b) Key to world chlorine versus caustic soda consumption.

and the US Gulf. Europe still has a caustic soda surplus which has declined over the last ten years. The USA exports both chlorine derivatives and caustic soda. Australia is a large importer of caustic soda, primarily for the alumina industry with a demand exceeding one million tons.

The changing balances which do occur have to be ‘resolved’. This can be by trade changes such as increasing exports of either EDC or caustic to balance the plant. Some markets are not easy to enter. For example, while Australia imports over one million tons of caustic soda it does so in 25 000 DMT shipments. This is 50 000 liquid tons of material. Relatively few plants have access to such facilities or can indeed store such a quantity. With some Asian countries becoming more self-sufficient in caustic production Japan had to increase its port handling facilities, raising the load size as well as increasing the number of ports to three.

1.5 The caustic return

Caustic soda prices vary with time. They usually cycle between \$30 and \$300 in the USA and from around DM300 to DM550 per Dry Metric Ton (DMT) in Europe. A

good return in caustic is vital to the industry. High-valued caustic implies low-cost chlorine. Caustic therefore has a 'price' whereas chlorine has a cost. Several companies have complex ways of transferring chlorine within the system, especially a company with many uses for chlorine. A useful way of looking at costs is to take the overall cost structure of the ECU, power, salt, labour, etc. and take out the return of 1.1 tons of caustic soda.

We show the 'cost' of chlorine in the case of caustic credits from export and domestic business (Figs 1.8 and 1.9). It is one of the many paradoxes in the business that although the plant is built for the chlorine, for most of the time the profit comes from the caustic soda. (Figure 1.10 shows the origin of the chlorine in the derivative trade.) The management of the caustic return is vital to the industry. The cyclicity in the demand for caustic with the supply will continue though the number of players in the business will probably reduce.

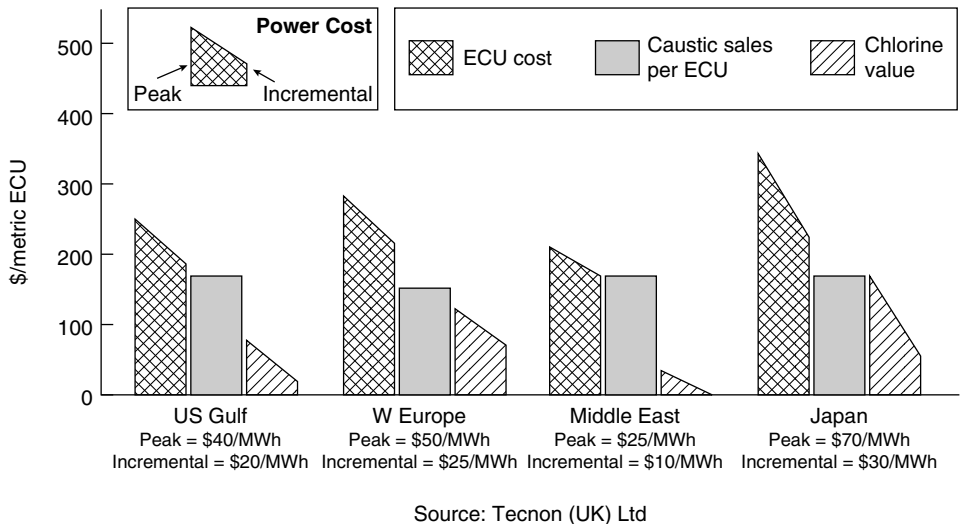


Fig. 1.8 Chlorine values from membrane cells as at the second quarter of 1999 based on exported caustic soda (to Australia).

The influence of distributors will probably increase as more companies are preferring to outsource the selling of the caustic. This then reduces the level of control that producers may have in the market. One area of control is of course the supply of caustic in the first place. Although at first glance the stoichiometry of the business suggests a rather rigid 1 ton of chlorine, 1.1 tons of caustic, there is nevertheless the hydrogen chloride or HCl calculation.

With more consideration being given to hydrogen chloride recycling it has been estimated that between one million and two million tons of HCl will be increasingly recycled. There are costs in using hydrogen chloride rather than chlorine but there are also benefits. If this hydrogen chloride is used rather than chlorine then the chlorine

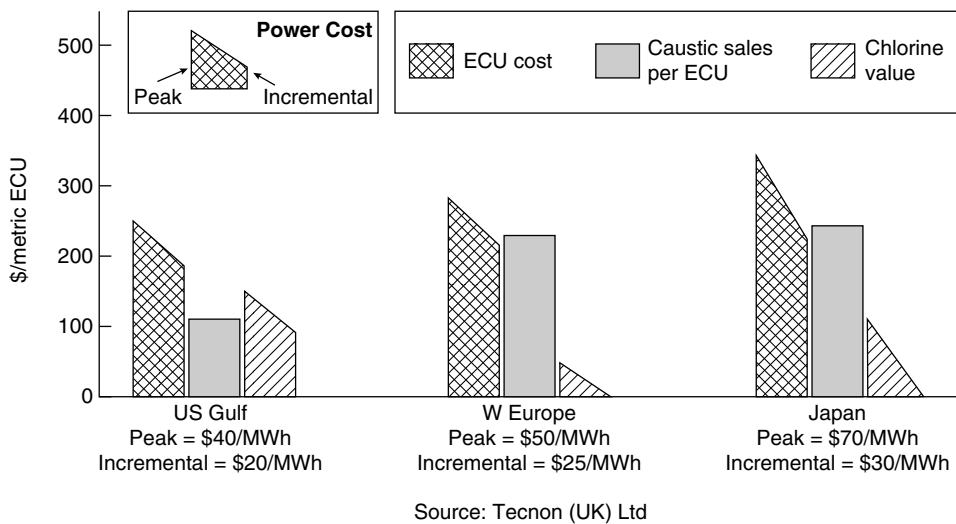


Fig. 1.9 Chlorine values from membrane cells as at the second quarter of 1999 based on domestic caustic soda. Thousands of tons of chlorine equipment.

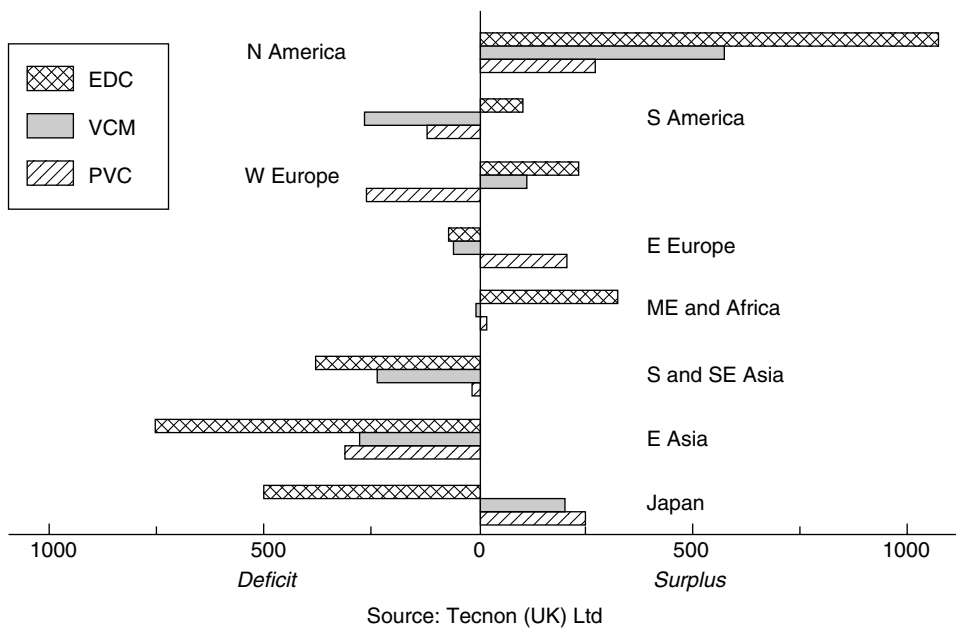


Fig. 1.10 Chlorine equivalent of net trade in EDC, VCM and PVC.

will not need to be made and this in turn means that caustic soda supplies would be tighter than otherwise would be the case.

Several chlor-alkali producers have some control over surplus caustic inasmuch as they use large quantities in-house. In some cases, if caustic is tight then the weak cell liquor can be upgraded and placed on the market. Dow's propylene oxide (PO)

system is a good example of this as the company could in theory use lime instead of caustic, though in practice it is only the Aratu plant in Brazil which can switch alkali. The caustic effectiveness of derivative production varies with the products and there is some scope for varying the alkali used internally, again with a view to controlling the supply.

Caustic pricing is becoming more global. In the past the domestic markets would have been immune from events elsewhere. Domestic surpluses could enter the deep-sea market with low prices without any impact on the domestic price. This is no longer the case. Some producers have been reluctant to dispose of caustic soda in the deep-sea market and have sought to sell in the home market by increasing market share. In the USA this has led to the two markets tracking each other and occasionally the domestic market is weaker than the contract market for Australia (see Figs 1.11–1.13).

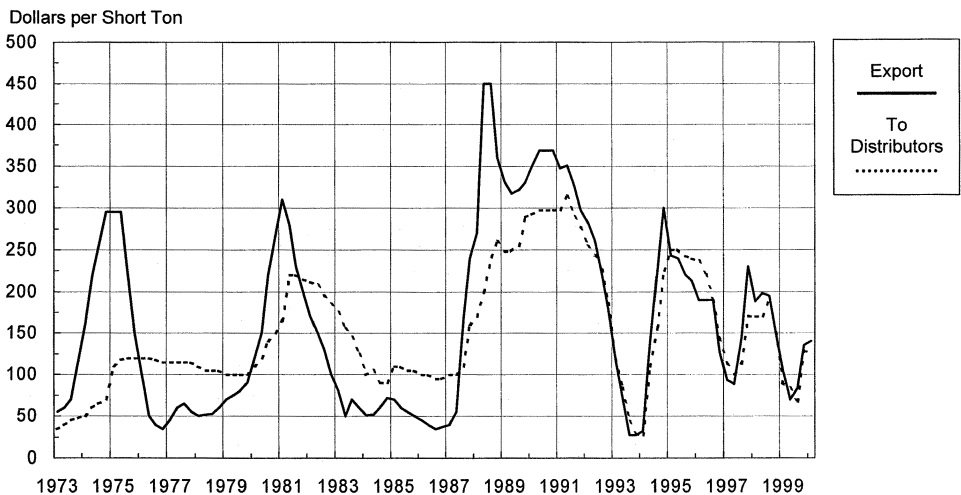


Fig. 1.11 United States export and domestic caustic soda prices. Source: Tecnon/Anorganica.

Europe too is now facing increasing pressure to offer international prices for caustic soda. There are indeed few markets currently where the domestic caustic market has immunity from caustic turbulence elsewhere though there are areas with freight advantages.

One of the most important contracts in caustic soda is the contract for the alumina industry in Australia. This is just over one million tons out of world production of about 44 million. Some have questioned why this contract should have an influence on the markets elsewhere. Although the Australian demand is a fraction of world demand the alumina price there is 'adopted' elsewhere, notably in the USA in the pulp sector and detergent sector. Thus a considerable part of the user industry is indirectly following events in Australia. In the past Australia has bought caustic soda from

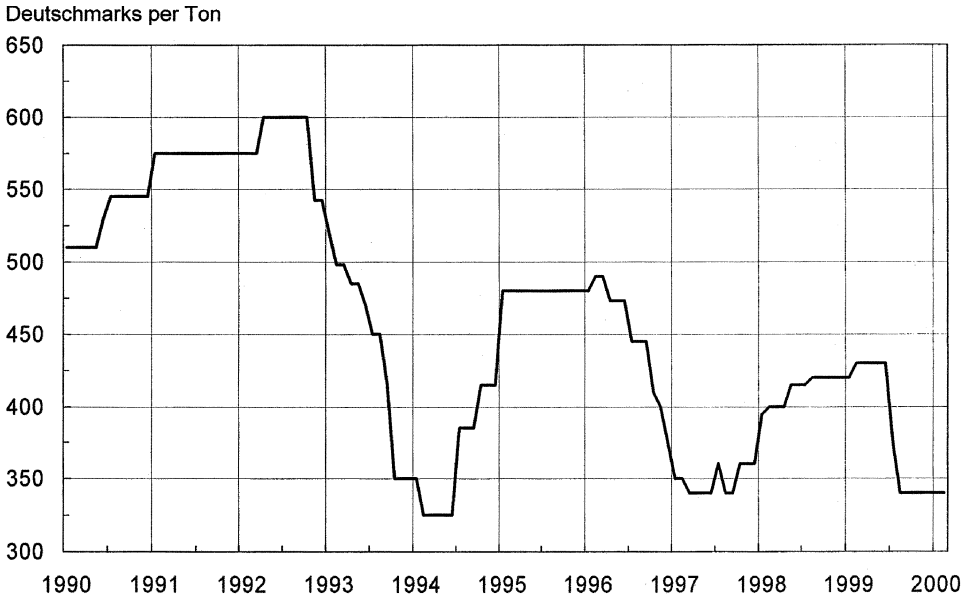


Fig. 1.12 West European caustic soda prices: liquid market (Germany only). Source: Tecnon/Anorganica.

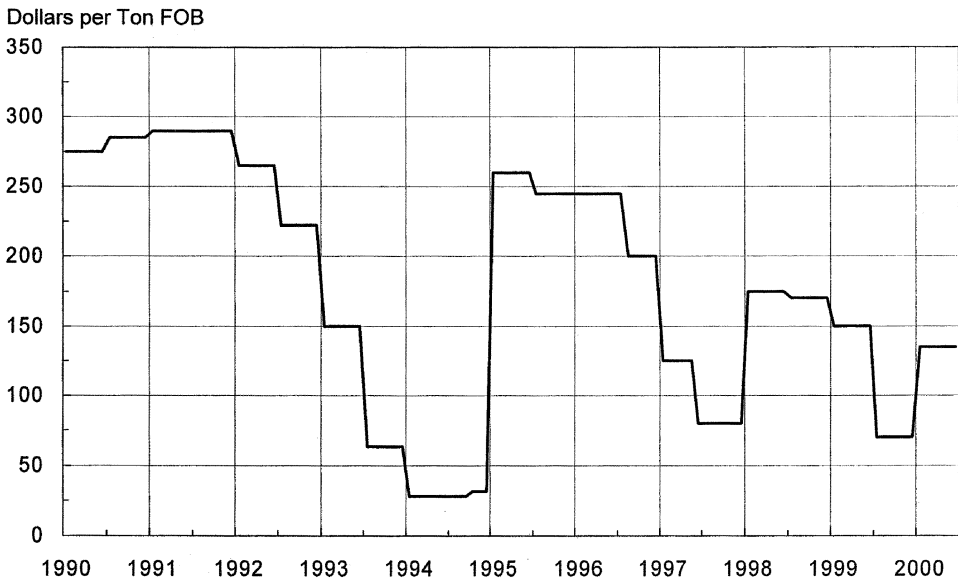


Fig. 1.13 Australian contract price excluding US Gulf. Source: Tecnon (UK) Ltd.

North America, Europe, Saudi Arabia and Japan. Europe has gradually dropped out of the contract. While Australia has bought from Korea and Indonesia from time to time the contract supplies are restricted to those countries mentioned above. That will change as the Qatar plant comes on stream in 2001. Should the Pilbara project in

Australia eventually be built then the whole trade issue will change once again with 'local' caustic being used in the alumina industry.

1.6 Diaphragm versus membrane

In Asia the membrane grade is standard. Japan is now totally membrane cell as far as caustic soda production is concerned (see Fig. 1.14). In Europe mercury cell predominates while in the USA it is diaphragm grade that predominates. Given that at some point membrane will grow to be the standard it is likely that some form of diaphragm discount will have to be offered in the future to maintain business. If caustic is long then diaphragm caustic will become increasingly difficult to sell. If caustic is tight and customers are desperate then a salt content would be overlooked.

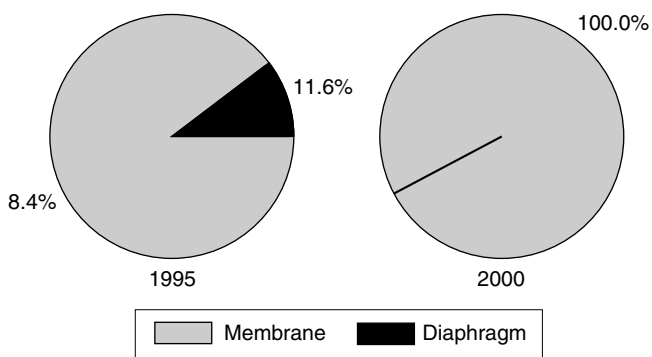


Fig. 1.14 Japanese caustic soda processes: 1995 versus 2000.

Source: Tecnon/Anorganica

In Australia one alumina producer has started to specify membrane-only caustic soda for consumption in the process. Yields of alumina production can be increased if membrane caustic soda is used.

1.7 Anhydrous caustic soda

The business has gradually declined with fewer producers in Europe making the product. At the same time capacity for prills has increased in the Middle East and in Thailand thus changing the delivered pricing in some markets. India has continued to expand capacity of flaked caustic soda and this production is now regularly quoted as far afield as South Africa. There are some expanding markets still in Africa and Asia but as these have been more geared to the new supply sources out of the Middle East and Asia it has become increasingly difficult for European suppliers to get a decent margin on the product. We expect this decline to continue

with more capacity in Europe being closed down. This can put pressure on inventory control for the liquid.

1.8 Ownership issues

Many chlor-alkali companies are changing hands and the degree of focus on chlorine is changing. As large mergers are being proposed in the cracker and refinery sectors, the chlorine unit does not come high on the list of priorities. Consequently several names are starting to disappear from the history books. ICI, Rhône Poulenc and Hoechst are three such examples. There will be more mergers in the USA, Europe and even Japan where major restructuring of the vinyl chain is now underway.

The aim of the restructuring will be to ensure competitive state-of-the-art vinyl units fed by either EDC or a state-of-the-art chlorine unit. Average plant sizes will increase, the number of producers will be reduced. However, this is still a long way off. Mergers in the vinyl chain have not always been easy. Both the OxyChem and Geon merger and the Solvay-BASF merger of interests were finalised after much discussion. EVC and Norsk Hydro fell fairly quickly and the Shell-Shin Etsu deal at Rovin took a long time.

On the customer side there are also changes as groups get larger. In the alumina sector there has been recent activity involving the consolidation in the industry with moves by Alcoa and Alcan in forming huge enterprises. These are subject to regulatory approval. In pulp and paper there has been gradual consolidation within the Nordic countries and in North America. In February two large transatlantic mergers in this sector were proposed. Gradually the number of large customers will decrease as will the number of suppliers.

Another trend in sales and marketing has been for the large multinational or transnational groups to favour single sourcing for a large part of the tonnage or at least to seek a supplier who can bid for all the business. This has been the case within the continental USA for some time and with the advent of the euro there is increased pressure for the large users to consolidate purchases in Europe if not on both sides of the Atlantic.

1.9 Chlorine demand changes

Many companies have said that if an alternative route to a derivative was economically justifiable that would be used in preference to a chlorine route. This has already had an impact on the technology of choice in some production routes to isocyanates, polycarbonate, propylene oxide and epichlorohydrin.

Some of the low-tonnage isocyanates are made without chlorine but this has yet to be proved for MDI and TDI. GE and Bayer have been adding polycarbonate capacity

without the use of chlorine. Dow has invested in Russian technology to make PO without chlorine and chlorine consumption can be cut in the epichlorohydrin process. Bayer and Lyondell are to co-operate in PO production.

These processes all vary in terms of the caustic effectiveness of the system as well as the implications on HCl generation and scope for recycling. It is really only PO and the isocyanates which would have an impact on the balance.

Environmental issues are discussed below. It is worth pointing out now that the industry has had to adapt to chlorine demand changes in this sector such as CFCs, pulp and paper and solvents. In Europe no chlorine is used in the pulp industry and it is being run-down elsewhere. Many of the plants which supplied chlorine into the pulp sector are situated a long way from other chlorine end-users and there have been closures of chlorine units, mainly in Scandinavia, Canada and the West Coast of the USA.

With PVC being the main driver for chlorine demand there is increasing pressure on the need to obtain cheap power, salt and ethylene feedstocks. Export-driven EDC and caustic plants have some place in meeting world demand though with the need to export both chlorine, in the form of EDC, and caustic soda there can be occasions when these plants are vulnerable to low returns if demand is much lower than supply. Traditional locations for these plants have been in the US Gulf and the Middle East, but there are plans to site such plants in Venezuela and Australia with both these countries having a large caustic soda demand in alumina.

1.10 Environmental restrictions

Many of the changes in chlorine consumption in the past ten years have arisen out of the environmental concern about the use of chlorine in some processes such as pulp and paper as well as the concern of the loss of the ozone layer with the use of CFCs.

These pressures have worked their way through the chain and now we have no chlorine consumption in pulp production in Europe and a much diminished consumption of chlorine in the HFC precursors. In addition the solvents sector saw a reduction in the demand for chlorine as many solvent applications changed.

There are restrictions in some countries on the surface movement of chlorine and this has forced some focusing of chlorine plant locations and shut down those with no or little captive consumption.

PVC still faces environmental pressure from two directions: there is hostility in the use of PVC in children's toys using the phthalate argument and building a new PVC complex faces severe regulatory pressure—witness the experience of ShinTech in the USA.

PVC and chlorine are still targets for environmental action. While there may be other targets for the environmental activists, such as GM foods in Europe, chlorine and PVC are still in the limelight for attacks on all fronts. No reason is predicted in the

industry for that to change and companies remaining in the chlorine chain will find that there will be a continued need to be seen to be using the best available techniques.

1.11 Chlorine: a utility or a product group

If the ideas described above are extended one can develop the 'Chlorine Park' concept. A chlorine park is a chemical complex with the supply of chlorine made by pipeline, HCl returns are made, other utilities are provided and the chlorine costed on a reasonable share of the revenues.

Several chlorine parks already exist. Geismar in Louisiana and Botlek in The Netherlands are good examples of these in operation today (see Figs 1.15 and 1.16). These sites are multi-customer based. The internal movements of chlorine and hydrogen chloride in a Dow site are also examples of a single-company chlorine park. Other, once single-owned complexes are splitting apart. The ICI complex at Runcorn could develop that way depending on who buys the chlorine chemicals business, the fluorochemicals business and how EVC develops. Several companies are seeking to attract users of chlorine to their site as there are moves to restrict chlorine transportation and this is one way of avoiding the movement of chlorine.

These are therefore some mechanisms for the development of chlorine complexes and the continued supply chain of chlorine through the derivatives. These also allow the increased use of HCl in the system and some control of the caustic supply.

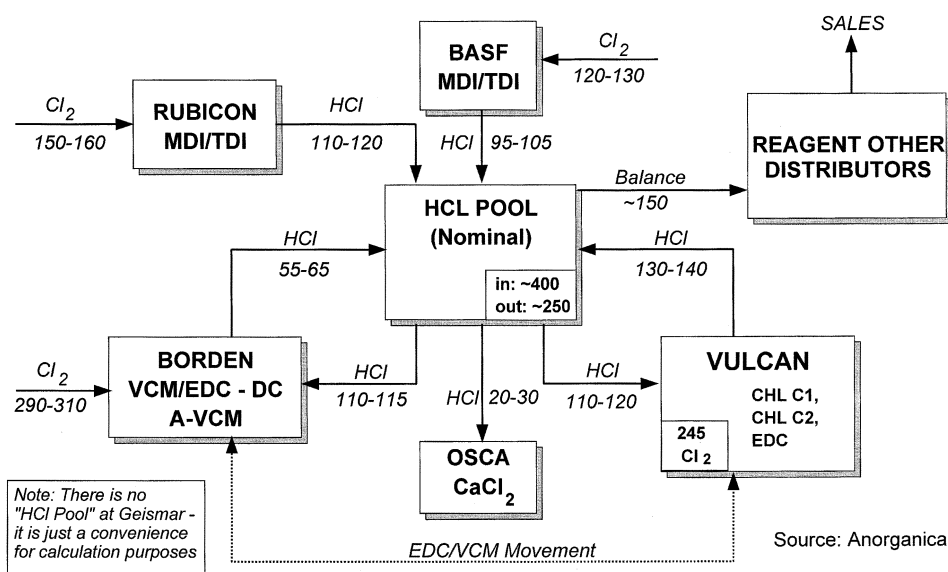


Fig. 1.15 Schematic of the 'chlorine park' in Geismar, Louisiana: 1996 appearance.

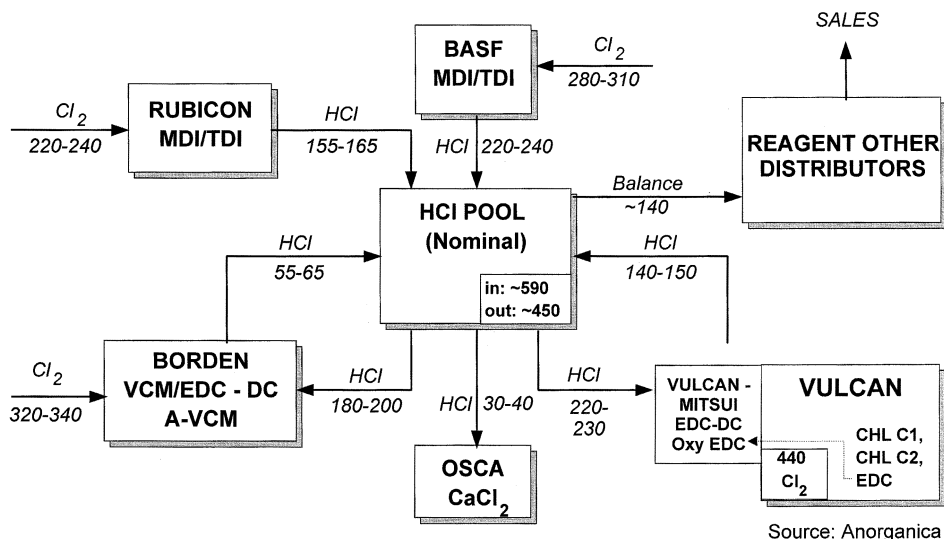


Fig. 1.16 Schematic of the 'chlorine park' in Geismar, Louisiana: 2005 appearance.

1.12 Conclusion

At the start of a new century it is possible to look at likely developments in the chlor-alkali business although there is some 'crystal ball' forecasting rather than usual market research employed.

Chlorine will still increasingly be used in the vinyl chain in spite of the anti-PVC lobby though there will be cost pressures. Changes in chlorine production locations mean a change in caustic trading patterns.

In the future it might be possible to see the gas diffusion technology generating chlorine with energy consumption at 1500 kWh. The chlorine will be used in the direct chlorination of ethane to feed the vinyl chain. Side streams of HCl will be used in oxychlorination where ethylene is available and this will use up by-product acid from isocyanates. Site integration will increase to benefit from economies of scale and optimise hydrogen chloride production.

The advent of e-commerce will have a profound effect on the marketing and pricing of caustic soda and some of the chlorine derivatives.

The industry faces many challenges. There are still savings to be made with the use of technology to meet energy consumption controls, environmental restrictions, economies of scale and profitability limits. There is also the need for the industry to attract good managers as producers have been attracted to 'life sciences'. I am sure a new entrepreneur of the calibre of a Solvay, Castner or Kellner will emerge in the next century.

Acknowledgements

The author wishes to thank Charles Fryer and Afzal Pradhan of Tecnon (UK) Ltd for help with the economics and diagrams and David Sherry of Anorganica for the chlorine and hydrogen chloride flows in Geismar.

Chapter 2

Phase-out Issues for Mercury Cell Technology in the Chlor-Alkali Industry

M Harris

2.1 Introduction

This chapter examines an issue that is one of the key determinants of the future of the West European chlor-alkali industry. It examines the environmental, economic, financial and political aspects of a debate whose effects are likely to spill over into North America and Asia – and to affect the development of the chlor-alkali industry world-wide.

The fundamental question is: should mercury cellrooms for the production of chlorine and caustic soda be phased out in the near future, or should the industry be allowed – on the basis of its existing voluntary commitment – to move away from this obsolescent technology as it reaches the end of its economic life over the next 20–25 years?

For over a hundred years the chlor-alkali industry has used the mercury cell as one of the three main technologies for the production of chlorine and caustic soda. For historical reasons, this process came to dominate the European industry – while in the United States the asbestos diaphragm cell took the premier position. Over the last two decades developments in membrane cells have brought these to the forefront, and membrane cells of one kind or another now represent the technology of choice world-wide.

Early mercury cells were a major source of mercury emissions to the environment – at levels which would be regarded as utterly unacceptable by today's standards. Concerns about mercury found a focus after 1959 when the Minamata Bay disaster in Japan was linked with organic mercury. This brought both public and regulatory concern to a level that demanded immediate action. In Japan this led to the progressive phase-out (completed by 1986 except for KOH production) of mercury cell technology with conversion to early versions of the membrane technology, which was just then becoming a practical option. Elsewhere the initial focus was on redoubling efforts to reduce emissions, discharges and losses of mercury from existing cellrooms – while accelerating the development of membrane technology for new cellrooms and,

potentially, for conversions. By the 1970s, regulators in Europe had begun to express concern at the level of mercury emissions from the chlor-alkali industry, and companies further accelerated their ongoing programmes of progressive emissions abatement.

Surprisingly, given the high profile of toxicity issues in the USA during the 1970s, the chlor-alkali industry came under much less regulatory pressure in that region. By contrast with Europe, where both asbestos diaphragm cells and mercury cells are now under pressure, the US industry has been far less under the regulatory microscope. In the USA there is little doubt that mercury cellrooms will be phased out as they reach the end of their economic life, but there is no reason to suppose that there will be any regulatory pressure to accelerate this change, nor on the asbestos diaphragm cellrooms that account for most of US capacity (Fig. 2.1).

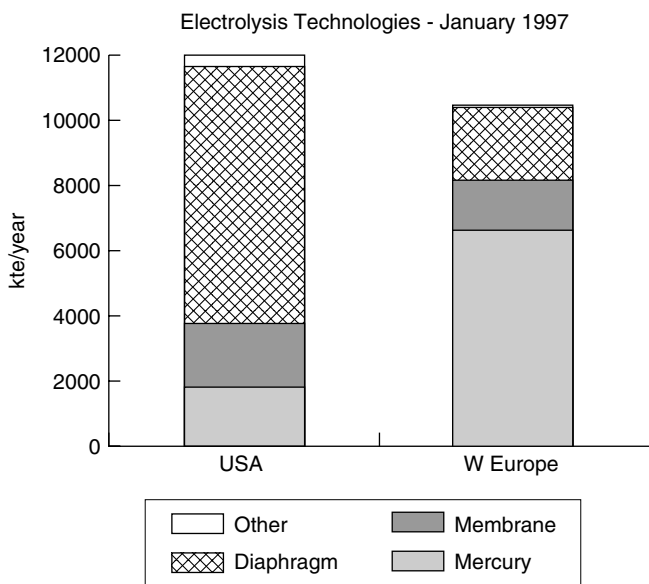


Fig. 2.1 Chlorine capacities by technology, USA and Western Europe, 1997 [1]. Source: Stanford Research Institute Consulting.

The rest of this chapter focuses on the European situation with regard to mercury cells. This seems appropriate, for not only is this probably the biggest single issue facing the European chlor-alkali industry today – threatening its very survival – but also there are lessons that can be learned from the way this issue has developed which are central to our understanding of the sort of chemical industry that will be allowed to operate in the twenty-first century. This is not only a European issue: the USA may have led the way in environmental regulation in the 1970s and early 1980s, but there has now been a role reversal. In the context of today's global economy, and in the era of multilateral environmental agreements of global scope, what happens in Europe today (whether it is progressive or simply paranoid!) is destined to happen in America and Asia tomorrow.

A fundamental question is raised for all stakeholders. Once emissions of a hazardous substance have been reduced to a level which causes no harm to human health or to the environment, is it wise to continue to spend scarce human and financial resources on reducing these particular emissions to zero – or should we prioritise the use of our skills and our money on other more pressing environmental goals? In other words, is the objective of environmental policy-making to reduce harm – as it should be – or to satisfy political goals in some sort of fashionable twenty-first-century ‘green’ iconolasty? European policy-makers, in particular, must urgently answer this question if we are to retain the manufacturing industries that are the primary source of financial and technological resources for the environmental improvements to which we all aspire.

2.2 Environment

2.2.1 Occurrence and sources [2]

Mercury is a naturally occurring element. Natural emissions of mercury, e.g. from ore deposits and from volcanic activity, are variously estimated at amounts between 2500 and 5500 tonnes/year and are thus similar in magnitude to anthropogenic emissions, which are currently estimated at some 3600–4100 tonnes/year world-wide. Some 30000 tonnes of mercury are readily available in the environment, i.e. in the atmosphere or in the mixing zone of the oceans, with tens of millions of tonnes in the upper layers of the continental masses and still more in the deep oceans (see Table 2.1).

Table 2.1 Natural and anthropogenic sources of mercury [3].

Typical quantity emitted into atmosphere (tonnes per annum)			
Natural sources		Anthropogenic sources ^a	
Windblown dust	50	Coal combustion	2100
Sea salt spray	20	Lead production	10
Volcanoes	1000	Copper/nickel production	120
Forest fires	20	Refuse incineration	1200
Continental particulates	20	Fuel wood combustion	180
Continental volatiles	610	Chlor-alkali ^b	7
Marine sources	770		
Total	2500	Total	3600

^a Mercury emissions to the atmosphere from landfills have not been included owing to lack of data.

^b This sector was not included in the published table, but was added at the request of the OSPAR INPUT group.

We can't do much about the volcanoes, but we do need to address the anthropogenic emissions. To do so, we need to know where these come from. Historically, there is no doubt that the chlor-alkali industry was one of the biggest anthropogenic sources. However, the industry has reduced its emissions by an order of magnitude and it no longer represents a major source. Annual emissions of the West European

chlor-alkali industry are currently just above 9 tonnes/year and falling, i.e. some 0.2% of anthropogenic emissions.

This does not mean that nothing need be done. For a persistent, toxic and bioaccumulating pollutant such as mercury, the goal of the industry must always be progressive emissions reduction to the lowest practicable levels. The industry has to aim towards zero – while recognising that this is by definition an unattainable goal. However, it does mean that it behoves governments to consider what can be done about the *major* sources while taking precautionary – but *proportionate* – measures towards minor sources such as the chlor-alkali industry. It is worth remembering, too, that today's concerns about mercury arise primarily from its role as a *global* pollutant, i.e. many of the most worrying adverse effects of mercury pollution are independent of the latitude and longitude of the source. At present it does seem that the West European authorities are devoting almost 100% of their efforts to just 0.2% of the problem.

2.2.2 Emissions

The key questions to be asked with regard to today's mercury emissions from the chlor-alkali industry are:

- (1) How much are these emissions?
- (2) How can they be reduced?
- (3) What risk do they present to human health or the environment?

In days past we would have changed the order of these questions and would have asked about the potential for harm to human health or the environment *before* considering emissions abatement. In those halcyon days it was deemed sufficient to be doing no harm. In Europe today, however, we operate in a society that has clearly set the goal of continuous emissions reduction towards zero – almost regardless of the consequences. We have finally reached so high a level of economic well-being that we set ourselves environmental goals on the basis of political rhetoric – 'zero risk', 'zero emissions', and even 'no hazardous substances'. Can anyone name a *non*-hazardous substance? Pure water is pretty life threatening by inhalation in the liquid state! Some highly hazardous substances – such as the antineoplastic drugs used in cancer therapy – are highly toxic and extremely hazardous. These goals are being pursued regardless of whether doing so abuses and destroys the resources that are needed to address the very real problems of twenty-first-century European society – social malaise, crime, personal, and public health, and education. And as for considering the developing world The quest for the holy grail of the 'Precautionary Principle' is being pursued with little sense of prioritisation or proportionality. If mercury is truly a *global* pollutant (and it is), surely we should be prioritising our resources towards reducing the large emissions from the developing countries and those with economies in

transition. The reported emissions last year from a single Siberian chlor-alkali plant seem to have exceeded the remaining emissions from all European plants from now until they are closed or converted!

Emissions from the European chlor-alkali industry

The European chlor-alkali industry has reduced its emissions dramatically over the past two decades. In 1977 the industry emitted 221 tonnes of mercury, equivalent to 27 grams per tonne of mercury cell chlor-alkali capacity (g/te). By 1998 this had been reduced to just over 9 tonnes, equivalent to about 1.5 g/te (Fig. 2.2). This represents a 98% reduction in losses in products, a 99% reduction in discharges to water, and a 91% reduction in emissions to atmosphere. There is probably not another major industry which can match these emissions reductions, so we can be forgiven for wondering why so much governmental time and energy is being spent on trying to accelerate the phase-out of mercury cellrooms – especially as the industry would be the first to agree that we will never even want to install new capacity based on this obsolescent technology. The mind of the regulator sometimes seems to be ‘a riddle wrapped in a mystery inside an enigma’.

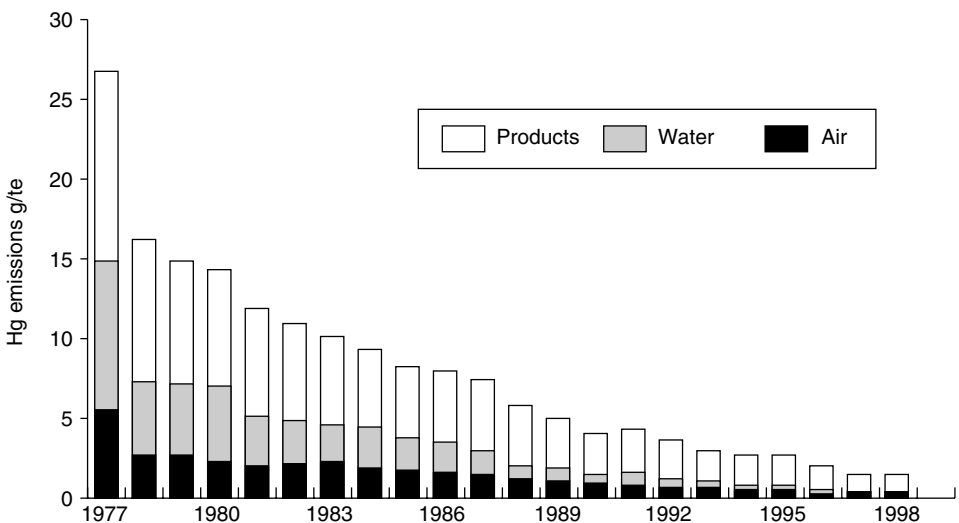


Fig. 2.2 Mercury emissions from the Western European chlor-alkali industry 1977–1998.

Emissions abatement

The industry continues its efforts to reduce even these emissions still further. The ‘law of diminishing returns’ does of course apply, and we are now reaching levels close to the limits of detection where it is difficult to be sure what measurements actually mean. At these very low levels there are also significant relative differences between

individual plants – arising from details of the process technology, details of construction, and even climatic conditions. Given that all West European plants are now operating to levels that present no threat to human health or to the environment, the yardstick is for each plant to do the best that it can in its own circumstances. We can rightly expect much more from a small modern enclosed plant than from a plant nearing the end of its economic life, soon to be shut down or converted, and perhaps even of open-sided construction.

For this reason, the industry has set its primary goals in terms of a capacity-weighted average for Western Europe. The Chief Executive Officer of each member company of Euro Chlor, the European trade association for chlor-alkali producers, has voluntarily and publicly promised that if plants are allowed to continue in operation after 2010, they will together achieve weighted average emissions of 1.0 g/te by the end of 2007 – a further 33% reduction over present-day levels – and will aim for 0.7 g/te by 2010. To put this in an international perspective, the US delegate to a 1997 UN/ECE meeting suggested a control level of 8 g/te – about double the level being achieved in Europe in 1990 when European regulators first introduced phase-out proposals.

Wastes

In northern Europe, at least, a further contentious issue is that of mercury-containing solid wastes – such as the sludges arising from normal operations as well as wastes arising on decommissioning and demolition of obsolete cellrooms. In most countries the regulators seem satisfied that these wastes do not represent transfers to the environment – except in a geological sense. Industry practice is thoroughly documented and is, of course, subject to approval and permission by national and local regulatory authorities. In most West European countries, all recoverable mercury is recycled from the wastes by retorting, and remaining residues are disposed of to appropriate registered landfill or other underground deposit, usually with some form of ‘inerting’ treatment (such as conversion to sulphide or encapsulation in mineral materials) in accordance with regulations appropriate to the particular levels of mercury remaining in the wastes. These regulated disposal practices are reinforced by a variety of monitoring programmes, e.g. for mercury in air or ground water in the proximity to the sites. Some countries, however, deem that even disposal to secure underground storage represents some kind of ‘emission’ to the environment – even though the procedures adopted actually represent returning the mercury to where it came from. It did after all start life as mercury ore that was mined and smelted – probably elsewhere in Europe!

Difference to balance

Mercury accounting is a non-trivial exercise as anyone who has ever been involved in its details will be well aware. It is intrinsic to the nature of chlor-alkali operations and

the accounting procedures adopted by the European authorities are such that a considerable amount of mercury *in any one year* has to be recorded as a 'difference to balance', i.e. a difference calculated by balancing mercury inputs and outputs from the plant.

This 'difference to balance' has three primary sources:

- (1) Statistical variation – mercury inventories in cells are so large, and emissions so small, that the calculations involving very small differences between very large numbers are inevitably subject to statistical error.
- (2) Accumulation in plant and structures – a considerable amount of mercury accumulates, e.g. in pipework, and can only be recovered and accounted for at the time of plant decommissioning (or possibly, in part, during maintenance and/or replacement of individual plant items such as pumps); studies suggest that over 90% of this mercury can eventually be recovered.
- (3) Reporting practice – reporting ceases when a plant no longer produces, so most of the mercury recovered during decommissioning is never recorded in the regulatory statistics and *appears* to have been 'lost'; this is simply a reporting artefact.

For many years the issue of 'difference to balance' caused great confusion in discussions between industry and the authorities. As a result of some detailed work completed in a co-operation between Euro Chlor and the OSPAR authorities [4], this issue is now much better understood by all stakeholders.

End-of-life issues

There is one further potential source of mercury emissions which, in fact, totally overshadows all discussion of emissions, discharges and losses but which, until recently, was not on the regulatory radar screen. There are about 12 000 tonnes of pure mercury contained in operating cellrooms in Western Europe. What happens to this mercury when the cellrooms close? After all, it represents some 1500 years of emissions at present rates from operating cellrooms, and it also represents some 15 years or more of global mercury production at present rates. Clearly the resolution of this issue is of importance not only for the environment but also for the mercury mining industry.

Some northern European authorities have proposed that this mercury be stored in deep mines in suitable geological strata. Somewhat inconsistently they also refuse to import or export mercury to allow this to happen. However, a moment's thought makes it clear that such deep-mine storage forces the mining and smelting of new mercury ore in order to satisfy the legitimate global mercury demand. It is ironic that over 50% of the world's mercury is mined within the European Union. The image of Sweden busily burying pure mercury while Spain is busily mining and smelting new

mercury from ore may well be grist to the mill of a future environmental cartoonist! Whatever happened to the recycling and conservation of resources?

Euro Chlor considers that a more rational and constructive approach is the one being developed in voluntary co-operation with the mercury mining industry. Proposals have been drafted based upon the concept that the cellroom mercury would be returned to the *mercury* mine and would replace, tonne-for-tonne, the mining and smelting of new mercury. This proposal would put to good use the existing mercury transportation and handling infrastructure, and would avoid adding new metallic mercury to the environmental inventory. The only outstanding difficulty appears to be the rate at which the logistical operations could be handled – probably no more than 400–500 tonnes/year. Efforts are being made to increase this, but it does seem that if all 12 000 tonnes are released within ten years – as would happen with a 2010 phase-out date – there will, sadly, be the need to resume mercury mining and smelting operations. On the other hand, if cellrooms are phased-out as they reach the end of their economic life, there is every possibility that mining operations in Europe can cease for some 20 years and then only resume at the much lower levels likely then to be required to meet a much smaller future global market. The choice, of course, rests with governments.

2.2.3 Environmental impact: conclusion

All recent studies, including detailed risk assessments carried out by Euro Chlor (the subject of Chapter 3), suggest that today's chlor-alkali operations in Europe do not present any risk to human health or the environment. Any further action would be based on a purely precautionary approach. The industry accepts that such further actions are required in the social and political circumstances of Western Europe today. It is committed to further emissions reductions, and to eschew the installation of any incremental capacity based on mercury cell technology. There are many scenarios combining emissions reduction and the decommissioning of existing plants. Any scientific analysis of the environmental merits and demerits of different scenarios has to start from the fact that, given the large amount of mercury in the environmental cycle and the slow rates of transfer to geological reservoirs (such as deep-sea sediment), the environmental measure of a phase-out scenario is not simply the *rate* of emission in any given year nor the *number of years* for which emissions continue until phase-out is complete. It is, rather, the convolution of these two parameters – the *cumulative environmental burden* – i.e. the *amount* of mercury added to the environment in the years preceding phase-out. The importance of this concept will become clearer as the phase-out strategy options are discussed in succeeding sections of this chapter.

However it is done, the conversion and/or closure of some 60% of the West European chlor-alkali industry is a major undertaking. The economic and social aspects are addressed next.

2.3 Economics

It is tempting for environmentalists to ignore economics and finance. After all, they say, the environment is more important than mere money. However, in the real world – where the rest of us live – we too want to improve and protect the environment, but this costs money and we recognise that without infinite resources we have to prioritise where we spend our money. We also recognise that if business does not make profits there will not be *any* money to spend! So I make no apology for addressing the economics of cellroom conversion.

Like all major capital investment projects, the financial case is based on the financial return, however measured, and the availability of finance.

2.3.1 Capital cost of conversion

There have been numerous estimates of the capital cost of cellroom conversion and inevitably these vary from plant to plant, even on a capacity-normalised basis. Even bigger variations in published estimates arise from the classical ‘boundary problem’ – what is included and what is not. Examples are legion and it is not the main purpose of this chapter to go into the technical and economic details of cellroom conversions. The capital cost of conversion for a typical mercury cellroom includes not only the cost of the electrolyzers but also, as a minimum base case, the inextricably linked capital costs associated with caustic recycle, caustic evaporation, brine secondary purification and dechlorination and additional gas cooling. In many cases additional capital will probably be required for new rectifiers (and possibly new electrical supply and switchgear), changes to the supply of utilities and gaseous HCl, new building structures, decommissioning and site remediation. Capital costs quoted in the literature range from below \$400 to above \$800 per tonne of chlorine capacity. (All costs are quoted in US dollars, not least as these are more or less equivalent to euros at the conversion rates of early 2000.) Enthusiastic suppliers of membrane cell equipment may quote at or below the bottom of this range – but this applies only to the cost of the electrolyser.

The calculation is further complicated inasmuch as trade-offs exist between capital and operating costs. Designing for operation at high current density can decrease the initial capital cost – but this increases operating costs and energy consumption. The development of lower voltage membranes is tending to shift the balance somewhat towards higher current densities – but will regulatory pressure on energy costs and energy consumption reverse this trend and increase capital costs?

In a typical practical conversion scenario, the capital required is likely to be in the region of \$400–700 per tonne of chlorine capacity. For the existing West European chlor-alkali industry this amounts to a capital investment of some \$3.2–4.8 billion. To achieve phase-out by 2010 this capital would have to be spent over the next ten years, i.e. at a rate of \$320–480 million every year for the next ten years. This is very

roughly equivalent to the total capital budget of the whole West European industry, i.e. there would be no restructuring and modernisation, no increase in capacity to satisfy growth in downstream markets, no significant maintenance of existing plants – and no capital expenditure on safety, health or environmental projects.

The industry is asking whether this is what even the most passionate environmentalist *really* wants – now that there is an unequivocal industry commitment to phase-out (on a sensible time-scale); now that mercury emissions have been reduced to a level which is harmless to the environment; and given that the industry does have important environmental improvement projects that it would like to carry out – is this a socially responsible and sustainable way of spending our resources?

2.3.2 Energy savings

It has often been claimed by proponents of rapid phase-out that the enormous capital costs of conversion are, at least, rapidly recouped through reduced operating costs and in particular through reduced energy consumption. This is a claim that seems far easier to make than to substantiate. There are indeed electrical energy savings to be made by conversion to membrane technology, and these savings have tended to increase as membrane technology has advanced. However, not only are these savings far less than has sometimes been claimed, they are considerably offset by increased energy requirements elsewhere in the process – most obviously if thermal energy is required for concentration of caustic liquor. As always, the exact balance will be highly site-specific. In fact the most important determinant of the presence or absence of energy savings and, if any, their size is usually the source of electric power to the site.

Various surveys of the literature reveal that on a like-for-like basis a typical conversion may achieve overall energy savings in the range 7–14% within site boundaries (see, for instance, Table 2.2).

A leading world authority on eco-profiles, Dr I. Boustead, has taken a much broader view of the energy comparison between the mercury and membrane technologies in a detailed study [5] of the energy economics of existing electrolysis plants. This analysis shows that membrane cell technology enjoys only a 7% energy advantage over mercury cells, with this probably being an overestimate as membrane cells are predominantly situated in countries using more efficient means of electricity generation.

Overall, the range of cost savings associated with conversion seems to fall between \$30 and \$50 per tonne of chlorine.

2.3.3 Financial case

A financial case will have to take account of capital costs, energy savings, certain other potential operating cost savings, and the cost of finance and taxation. Again the

Table 2.2 A comparison of energy consumption: mercury versus membrane.

	Mercury technology	Membrane technology
Theoretical voltage (V)	3.15	2.19
Cell voltage (V)	3.9–4.2	3.0–3.6
Current density (kA m ⁻²)	8–13	3–5
Caustic strength (wt %)	50	33
AC electrical power consumption (kWh tonne ⁻¹ Cl ₂)	3360 at 10 kA m ⁻²	2750 at 3.6 kA m ⁻²
Other electrical power consumption (kWh tonne ⁻¹ Cl ₂)	200	140
Steam consumption for caustic evaporation (kWh tonne ⁻¹ Cl ₂)	0	180
Total energy consumption (kWh tonne ⁻¹ Cl ₂)	3560	3070

precise details will be highly site-specific. However, in general terms – and considering a very wide range of scenarios – the basic financial parameters for mercury-to-membrane conversion fall within a fairly well-defined envelope. If attempting to accommodate the wide published range of estimates, the financial case could be examined with capital costs in the range of \$400–700 per tonne of chlorine, operating cost savings in the range of \$30–50 per year per tonne of chlorine and discount rates in the range of 8–14%. Conventional financial modelling then gives the range of net present values (NPVs) displayed in Table 2.3.

Table 2.3 Financial parameters: mercury-to-membrane conversion^a.

Capital cost of conversion (\$m per tonne of chlorine capacity)	Operating cost savings from conversion (\$ per year per tonne of chlorine capacity)	Discount rate (%)	NPV (\$m)	
			Best case	Worst case
Range: 40, 55, 70	40	12	–10	–37
55	Range 30, 40, 50	12	–16	–29
55	40	8–14	–11	–26
40 (best) or 70 (worst)	30 (worst) or 50 (best)	8 (best) or 14 (worst)	+6	–38

^a Calculations cover a range of plant operating life from 10 to 40 years and are for a notional 100 000 tonne per year cellroom.

From the results it can be seen that the value of the project is negative for virtually all cases. Only with discount rates below 10% can the financial case be forced above zero – and then only if the lowest conceivable capital cost (\$400 million) and the highest conceivable savings rate (\$50 per year) are simultaneously assumed. Discount rates for major capital projects in the chemical industry are currently 12% or more, and higher (15%+) for high-risk projects. And remember – the project would not result in any measurable environmental improvement.

Why then are conversions carried out at all? The answers are of course quite simple. As a mercury cellroom reaches the end of its economic operating life – typically after some 40–50 years of operation – it has either to be replaced or closed. And any state-

of-the-art replacement means conversion to membrane technology. There is, of course, some variability as to the economic life of a plant on a case-by-case basis. The precise timing of conversion (or closure) will depend on a company's overall strategy, its portfolio of manufacturing operations, its market portfolio of downstream users of chlorine and caustic, the extent to which it is integrated and can achieve in-house economics, its vision for its position in an industry which – above all in Western Europe – is undergoing radical restructuring and rationalisation. It will also depend on the availability of capital for the project – in competition with other demands on capital within the corporate survival strategy.

In short, conversions are carried out either when the existing cellrooms are worn out and *have* to be replaced, or as part of an overall restructuring and expansion of a company's operations in which context a viable financial case may exist and funds may be forthcoming. Conversions (or, in their absence, closures) will occur progressively over the next couple of decades or so as the European industry modernises and improves its international competitiveness. It is questionable whether any amount of governmental pressure can significantly accelerate the rate of cellroom conversions; however, governments *can* so act as to force closures *instead of* conversions – with all of the social and economic consequences that would entail.

2.3.4 Macroeconomic effects

Having raised the issue of forced closure, it is worth taking a quick look at the wider economic consequences. Macroeconomic effects are notoriously difficult to predict, and the biggest consequences of the closure of up to two-thirds of the West European chlor-alkali industry will be felt through the knock-on effects on downstream industries – which would then have to compete in extremely tight markets for imported caustic and EDC. In fact it is more likely that many of the primary customers of the chlor-alkali industry – in particular the PVC chain – would themselves gradually migrate away from Western Europe to be closer to sources of supply. There would thus be a continuing effect over decades to come as products further and further downstream from chlorine would have to be imported into Western Europe instead of manufactured domestically. The macroeconomic and strategic consequences of Western Europe gradually abandoning its manufacturing base and becoming increasingly dependent on the service industries would be a subject for an interesting, if depressing, book but not for this chapter.

More directly and in the shorter term there will be consequences for employment. As a capital-intensive industry, the chlor-alkali sector itself does not employ large numbers of people. However, the indirect employment consequences of closure are much greater. Industry estimates may be seen as being too well informed and therefore unreliable, and instead it might take governmental estimates. The European Commission (DG-III, now DG-Enterprise) has estimated that there would be a loss of 10 000 jobs in the EU chemical industry by the year 2010 – *ignoring secondary effects* [6]. The

German government has recently informed OSPAR that there are 6650 employees in the German chlor-alkali industry (which is currently based 50% on mercury technology), with 250 000 jobs (in Germany alone) dependent on this industry [7].

Quantification of the macroeconomic effects of cellroom closure is extremely difficult. But it is significant that this difficulty arises precisely because the chlor-alkali industry forms the base for such a large proportion of so many diverse sectors of manufacturing industry – and thus of the tax base for national governmental budgets.

2.3.5 The OECD analysis

There are many people today who argue for integration of environmental considerations into commercial and financial planning by means of some form of environmental accounting that attempts to measure the positive and negative environmental effects of economic activity. This is certainly a most worthwhile – although difficult – goal. One of many inputs to such calculations is risk–benefit analysis, a variant of cost–benefit analysis which examines the trade-offs between the benefits and risks of an activity. At today's mercury emission levels there is unlikely to be any health or environmental case at all, so in order to conduct a worst-case analysis a look back into history is needed. One such case study exists and was presented in January 1998 to the OECD [8] by academics in Japan who carried out such a study after the completion of the conversion of all major mercury cellrooms to membrane in the aftermath of Minamata. This study calculates the benefit–risk ratio (BRR, i.e. the ratio of costs divided by risk abatement) for various scenarios, using loss of life expectancy (LLE) as a means of comparing various kinds of health risks. The study concludes that 'the government decision on the prohibition of the mercury electrode process was far from cost-effective ... if the replacement of the mercury process had been implemented when the industry renewed existing plants, the value of the BRR would have been markedly decreased. ... to prevent development of such an extreme policy, the government must abandon the zero-risk position ...' The study calculated the most probable cost of an increased life expectancy of one life-year at \$57 million, and compared this with other Japanese environmental health policies which fell in the range \$0.24–0.45 million per life-year, and with US EPA toxic control policies, estimated at \$4.2 million per life-year.

The results speak for themselves. There is neither an environmental nor an economic case for accelerating mercury cellroom conversions beyond the time-scale of 20–25 years to which the European industry has already expressed its commitment. The only rationale is 'political' – which brings us to the final section of this analysis.

2.4 Regulation

Thirty, twenty – even ten – years ago there was an environmental case for much stricter regulation and control of emissions, discharges and losses of mercury from the

chlor-alkali industry – even in Western Europe. Industry was meeting the regulations that existed at that time, and had adapted its working practices to eliminate significant risks to human health. But there had not been a full response to the concerns that were beginning to be expressed about possible environmental effects – particularly those effects that could take place far distant from the plants themselves. The era of the global pollutant was dawning – concerns about the stratospheric ozone layer were to lead to the Montreal Protocol – but we were slow to extrapolate. Most of today’s regulatory activity – however unnecessary and misdirected it may *now* be – has its origins in the concerns of this past era. If we regret the regulatory excesses of today, we must also consider our own past short-sightedness that helped push the pendulum to the other extreme.

There is a striking lesson for industry to learn: it is not sufficient to comply with regulation – the industry needs to anticipate regulation by assessing the potential for harm from its activities and taking voluntary action without waiting for governments to react. For when they do, if there has been no action governments are more than likely to over-react. We have called this approach Responsible Care, environmentalists call it the Precautionary Principle; we might both compromise – at least on the rhetoric – and call it Sustainable Development. Be that as it may, in Western Europe chlor-alkali now faces regulation in at least three major international arenas.

2.4.1 UN/ECE

In response to growing concerns about air pollution that could cross national frontiers and produce adverse effects far from its source, the United Nations Economic Commission for Europe (UN/ECE) developed its 1979 Convention on Long-Range Transboundary Air Pollution. For historical reasons, the geographical scope of UN/ECE covers – despite its name – not only the whole of Europe (including all of the territories of the former Soviet Union) but also the United States and Canada. Protocols to this Convention cover pollution from sulphur dioxide, nitrogen oxides, volatile organic compounds (VOCs), persistent organic pollutants (POPs) and heavy metals (at present, cadmium, lead and mercury). The Heavy Metals Protocol [9] (signed in Aarhus in 1998) considers the chlor-alkali industry as a significant source of mercury emissions. In some of the territories with economies in transition, this is still certainly the case.

The Protocol requires *inter alia*:

- (1) the implementation of effective emission reduction measures from 1990 levels;
- (2) the application of Best Available Technology (BAT) by two years (for new plants) or eight years (for existing plants) after entry into force of the Protocol – this probably means by about 2004 and 2010, respectively; and
- (3) the application of emission limit values (ELVs).

For mercury cellrooms it expects that the application of BAT will result in emission levels well below 2.0 g/te (of chlorine capacity) and notes that there are examples of plants achieving levels well below 1.0 g/te. Numerical emission limit values were set at 0.01 g/te for new plants (deliberately equivalent to a ban on mercury technology) but will not be decided for existing plant until two years after the Protocol enters into force (say, by 2004).

The standards set by this Protocol are in fact already met by all West European chlor-alkali plants and the West European producers had already voluntarily committed to eschew mercury technology for new plants. The main value of the Protocol is in setting challenging standards to be met by the producers in Eastern Europe – particularly in the countries of the former Soviet Union where emission levels were recently, in some cases, still more than 50 times higher than required by the Protocol. It also has value in setting a level playing field as between North America and Europe.

2.4.2 IPPC Directive and the chlor-alkali BREF

In the European Union the key instrument governing the prevention and control of pollution is the 1996 IPPC (Integrated Pollution Prevention and Control) Directive [10]. Member States were required to implement this Directive through national legislation and regulation by September 1999.

The Directive is founded firmly in the concept of BAT (Best Available Techniques) – which is painstakingly defined in the text. Although the Directive does not set emission limit values *per se*, it does have procedures which set out the quantitative levels of emissions that can be expected to result from the application of BAT. The subtlety of this approach allowed all Member States to agree the Directive – but has led to considerable debate thereafter in terms of the balance of powers between the local competent authorities (who can, and usually do, set emission limits on a plant-by-plant basis) and the European Commission which is the guardian of BAT as set out under the Directive.

The practical implementation of the Directive takes place by means of the development of a series of BAT Reference Documents (BREFs) which serve as guidance documents either for individual industrial sectors (such as the chlor-alkali industry) or, in the case of the so-called ‘lateral BREFs’, for cross-cutting activities.

The development of the BREF for the chlor-alkali sector began in December 1997 and until late 1999 proceeded both very slowly, and to some extent without a full understanding of the technical complexities of chlor-alkali production. It was perhaps therefore unsurprising to find that the recommendations were also that BAT was defined as membrane technology not only for new plant (which is entirely reasonable) but also for existing plant. This would have been tantamount to plant closure by around 2008 – at least in those several countries that were misinterpreting ‘BAT’ as a uniform obligation rather than as guidance for local regulators making plant-by-plant decisions on permission.

In late 1999 and early 2000, however, a much improved and accelerated technical dialogue took place. This has resulted in a recent third draft of the BREF [11], which was broadly accepted by a meeting of the Technical Working Group in Seville in March 2000. Further detailed work is required, but there is now hope that the BREF will be completed in Summer 2000 as a consensus document between the industry and its regulators and go forward to the September 2000 meeting of the Information Exchange Forum (IEF) for adoption at the political level. The BREF will then act as guidance for, and a very strong influence on, national regulators. The industry must expect – as a minimum – increasing pressure towards early conversion of the remaining mercury cellrooms, and in many cases the imposition of very challenging emission limits (albeit taking some account of individual plant circumstances). Initial enthusiasm for goals as low as 0.2–0.3 g/te (representing the best that can be achieved by plants which have been appropriately built and designed from the start, and are operating under the most favourable local circumstances) has been moderated, but pressures towards levels well below 1.0 g/te are inevitable.

2.4.3 OSPAR

‘OSPAR’ is perhaps the best known – and most powerful – of several marine environmental protection conventions operating within European and adjacent waters. The OSPAR Convention, properly known as the Convention for the Protection of the Marine Environment of the North-East Atlantic [12], was opened for signature in September 1992 at the Ministerial Meeting of the Oslo and Paris Commissions. Its Contracting Parties are those countries with territories draining into the north-east Atlantic, i.e. all of the European Union Member States except Austria, Italy and Greece, together with Norway, Iceland, Switzerland and the European Commission. Formed and largely managed by the environmental ministries of the Contracting Parties it lacks the balance provided in EU legislation by the need to obtain agreement between environment, trade and industry and other directorates. Initially it was also characterised by a lack of transparency unusual among European institutions inasmuch as NGOs (whether environmental or business) were excluded from its meetings – even as observers. This was all the more unfortunate because OSPAR does have significant legislative powers – although the conflict between these and those of the European Union to which most OSPAR Contracting Parties belong continues to give rise to complex and occasionally fractious debates. Since 1998, however, there have been significant improvements in the operation of OSPAR. Its considerable activity has attracted participation from other departments of government, and it has opened its doors to NGOs as observers. These changes have had the twin benefits of improving the credibility of OSPAR as an organisation and of improving the quality of its decision-making by incorporating factual technical information before rather than after rule making.

Mercury and its compounds are toxic and persistent and have a marked ability to

bioaccumulate. Accordingly, even though mercury is naturally occurring, mercury pollution has always been quite high on OSPAR's list of priorities. The chlor-alkali industry, in part because of its less than pristine past and in part because the chemical industry is always an easier target than the more significant mercury sources (most combustion processes, including most power generation and incineration), has come in for a great deal of attention.

Early regulation focused on discharges to the aquatic environment. These decisions and recommendations have been largely overtaken both by more stringent EU legislation and by industry abatement efforts, which have so reduced mercury discharges directly to the hydrosphere that they are rarely an issue. By 1990 attention had turned to the atmospheric emissions from the chlor-alkali industry that were still, at that time, unacceptably high. Decision 90/3 of the Paris Commission (one of OSPAR's two precursors), taken in a closed meeting (with industry observers excluded) in 1990, stated *inter alia* that:

- (1) 'mercury based chlor-alkali plants shall be required to meet by 31 December 1996 a standard of 2 g/te ... for emissions to the atmosphere..., and
- (2) [Contracting Parties] RECOMMEND that existing mercury cell chlor-alkali plants be phased out as soon as is practicable. The objective is that they should be phased out completely by 2010.'

The first requirement has already been met and exceeded. The contorted legal language of the second requirement has, however, led to considerable debate – it being a 'recommendation' contained within a 'decision'. Whatever the legal force of this part of PARCOM 90/3, it has considerable political impact and most Contracting Parties feel the need to honour the spirit of the Recommendation. Unfortunately, differences in national interpretation are hardly conducive to a 'level playing field' within the European Union (a basic tenet of the founding Treaty of Rome) – and certainly give rise to considerable confusion within industry.

These uncertainties and differences in interpretation would be less important were it not for the environmental and economic aspects of the issue described in preceding sections of this chapter. If the Recommendation were honoured to the letter and all OSPAR area chlor-alkali plants were to be forced to close or convert by 2010, we would see no environmental gain but considerable economic and social damage. EU lawyers might also like to consider the situation for major producer countries like France and Spain where some of their plants are within the OSPAR catchment area and others – with drainage to the Mediterranean basin – are not!

Because industry was completely excluded from the deliberations that led to the 1990 decision, it was perhaps somewhat slow to recognise that the challenge imposed by PARCOM 90/3 was a life-or-death matter. Huge strides were made, as described above, in emissions abatement; conversions – and some closures – continued. But by

the second half of the decade it was clear that the 2010 target was quite impossible – at any price – and would no longer provide any environmental improvement. Some governments also began to feel increasingly uncomfortable with the 1990 decision. Fortunately the OSPAR process provides for a mandatory ten-year review of decisions and recommendations – and it is now the year 2000.

The first operational decision by OSPAR was a typically governmental action – to postpone any review of PARCOM 90/3 until 2001. Unlike industry, government makes the rules and can thus delay its compliance with them! But the issue is now attracting a great deal of attention within OSPAR from most member governments. A particular piquancy is given to the debate in the light of the elevation of mercury and its compounds in 1998 to OSPAR's list of 15 'Priority Substances' and the announcement in the same year by OSPAR Ministers of the 'Sintra Statement' [13] which includes the text:

'... We agree to prevent pollution of the maritime area by continuously reducing discharges, emissions and losses of hazardous substances ... with the ultimate aim of achieving concentrations in the environment near background levels for naturally occurring substances and close to zero for man-made synthetic substances. We shall make every endeavour to move towards the target of cessation of discharges, emissions and losses of hazardous substances by the year 2020 ...'

Once again, the lawyers have been at work and – as written – the Sintra Statement represents an important and valuable 'mission statement'. Unfortunately it is already being widely misinterpreted as a binding commitment to an 'elimination objective' or even as legally binding Contracting Parties to a zero emissions regime by 2020. In this form it is permanently unachievable and were it law it would be exceedingly bad law as it would be totally unenforceable. Worse still, attempts to enforce it would close down most of Europe's manufacturing industry.

The serious consequences of this misinterpretation have already become apparent in the legal and procedural difficulties currently existing with regard to the European Union Water Framework Directive – where the European Parliament has lost sight of the subtleties of Sintra and demanded a legally binding commitment to zero emissions by 2020. This has led to the unseemly spectacle of Governments, advised by their lawyers, saying that when we said 'eliminate' we didn't really mean 'zero'. So the first attempt by Parliament to exercise its greatly enhanced powers under the Amsterdam Treaty has fallen far from the intended heights of democracy. Hopefully OSPAR will learn by example.

In the last three or four years, industry has risen to the challenge presented by PARCOM 90/3. The response has been on two fronts. On the one hand industry is trying within the OSPAR process to assist in making sure that the way in which it interprets and implements the decision is as favourable as possible to the environment without doing permanent and unacceptable economic and social damage. On the

other hand, recognising our responsibility to minimise the environmental impact of our operations, we have offered six voluntary commitments.

Working within OSPAR

Once OSPAR had recognised – at the 1997 Commission meeting – that there were some real problems over the interpretation and implementation of PARCOM 90/3, it became possible for industry to embark upon a process of explanation of what it had done to address the concerns raised – and, equally, what remained to be done and how it was being tackled. Through its trade association, Euro Chlor, the industry developed a strategy to deal with mercury plants during the remaining years of their operational life and – importantly – during and after their conversion and closure.

Based upon extensive scientific studies carried out in collaboration with a number of universities and international experts, Euro Chlor was able to recognise that:

- (1) emissions levels had now so decreased that it was extremely unlikely that they could now have any environmental impact at all, and that even if they did,
- (2) any environmental impact was dependent on the cumulative amount of mercury emitted from the present day until the conversion/closures were complete (see Section 2.2.3).

This provided the underpinning for a shut-down strategy for the existing mercury cellrooms. Euro Chlor's challenge was to achieve further emissions reductions sufficiently great that – even with the exit from mercury carried out as plants reached the end of their economic life – the cumulative mercury burden would be less than the best that could be achieved under the 2010 phase-out scenario. This was not easy, but it did rapidly become clear that 2010 phase-out was not only unlikely to be achievable in practice but that any attempt to achieve it would divert resources completely away from any further emissions abatement efforts. In practice, therefore, there would be trade-off between emissions abatement and closure dates. The details of this were established through independent studies carried out by SRI Consulting [14] who developed a model – detailed down to the level of individual plants – for the progressive exit from mercury technology. By combining this model with known emission levels, again on a plant-by-plant basis, it was possible to calculate mercury burdens for different scenarios.

All of this work went on in parallel with the development and implementation of best practice in every aspect of the operation, decommission and demolition of mercury cellrooms. Particular attention was paid to the atmospheric emissions, which now dominate, and subsequently to a range of complex issues concerning waste disposal and, not least, the appropriate fate of the 12 000 tonnes of pure mercury contained in operating cellrooms.

OSPAR facilitated these technical efforts by setting up an Intersessional Correspondence Group (ICG) – a loose group of experts drawn from industry and government – which reports to OSPAR's annual meeting on point sources of pollution (known, creatively, as POINT). This work culminated in a two-day chlor-alkali workshop ('WOCAP') in Madrid in September 1999 at which very full technical presentations were made on every aspect of the mercury issue. The conclusions of this workshop supported some, but not all, of industry's views. Where areas of technical disagreement still existed these were referred back to the ICG for resolution.

The POINT meeting in Seville in December 1999 debated, and broadly endorsed, the findings of the expert Workshop. POINT renewed the mandate of the ICG to continue its detailed studies on the most environmentally favourable and practicable way of implementing PARCOM 90/3. In parallel, the more political issues were to be referred upwards within the OSPAR hierarchy to its Programmes and Measures Committee (PRAM) meeting in Calais in April 2000. The PRAM meeting in mid-April was the first real discussion within OSPAR at the political level of the possible need to revisit the implementation of PARCOM 90/3. It was therefore unfortunate that many governmental delegates had clearly – even by their own admission – received no briefing from their more technical colleagues on the outcome of the discussions at WOCAP and POINT, nor of the detailed studies carried out by the ICG, nor of the potentially high political stakes. The result was an initial proposal to refuse to consider any updating of the 1990 decision followed by a difficult ensuing debate. However, after consultations with capitals and extended bilateral discussions, PRAM eventually decided to continue the mandate of ICG and to continue work to determine the best way forward. It was made very clear that any revised proposals would need to show a net environmental gain (as does the Euro Chlor proposal). Several countries wished to embark on national studies of the environmental and/or socio-economic consequences of various scenarios (France and the UK already have work in hand). These studies, while useful, will unfortunately cause delays in the decision-making processes of OSPAR. It is now foreseen that the earliest date for a decision will be the OSPAR Commission meeting in the summer of 2002. This delay will act as something of a 'planning blight' for the West European industry as it contemplates the bigger picture of its much-needed rationalisation. Ironically, a delayed decision will tend to cause delays in cellroom conversions because of continued uncertainties about the investment environment. Indeed, by 2002 it seems rather unlikely that there will be enough time left to convert the then remaining mercury cellrooms by 2010. This will be as much by reason of the non-availability of engineering resources, and perhaps even of membrane cells, as by reason of the non-availability of adequate capital funding from banks and shareholders. Meanwhile the industry will, of course, continue its efforts towards emissions abatement and, where practicable, technology conversion.

Six voluntary commitments

One of the key developments in building an improved and constructive relationship with the OSPAR authorities has been the increasing recognition by industry that it is necessary – but *not sufficient* – for our strategy to be based firmly on sound science and technological common sense. Whether we like it or not, people are not logical and are not well-informed about matters scientific and technical. The real world is multifaceted: attitudes and decisions are based on a far wider range of perceptions and emotions. Politicians – and, through them, the regulators that serve them – represent the real world and respond to this. They may do it well, or badly. We may like it, or not. But the fact remains that our industry has no future unless our strategic approach to the sustainable development of our industry takes account of public concerns. Where these are founded in ignorance we may try to inform. But we must do much more than this: we must build *credibility* so that our information is accepted. Building credibility requires listening and taking action.

It is for this reason that the Chief Executive Officers of every West European chlor-alkali producer have, through Euro Chlor, entered voluntarily into six binding commitments [15]. All but one of these are unconditional. In this sense they do not represent part of some kind of negotiation; rather, they are an attempt to demonstrate by action that the industry, whatever its past, is now totally committed to addressing public concerns about its use of the mercury process. It matters not that these concerns are almost entirely without foundation: they are there, and we have to address them.

The ‘Madrid Commitments’ were announced at the OSPAR workshop in Madrid in September 1999. In summary they are:

- (1) There will be no increase in mercury chlor-alkali production capacity. This is an unequivocal reiteration of a commitment made in 1995. It represents a *de facto* commitment to phase-out as mercury cellrooms reach the end of their working life.
- (2) Mercury cells will not be shipped to third parties for re-use. This provides reassurance that the technology will not simply be moved outside of Western Europe.
- (3) Mercury emissions will be reduced. Although all of the requirements of PAR-COM 90/3 in this respect have already been met, the companies commit to going further and to continuous improvement. This commitment has to be conditional as the considerable capital required will not be available if the companies are forced to close their mercury cellrooms by 2010. But assuming that OSPAR recognises that this is an unachievable goal and that cellrooms are allowed to continue in operation beyond 2010, plants will achieve a weighted average emission level better than 1.0 g/te by the end of 2007 and aim to achieve levels better than 0.7 g/te by 2010. The commitment is made on an industry-wide basis because it is recognised that because of the different circumstances of each plant,

application of BAT will achieve different quantitative emissions outcomes on different plants. There is a further commitment that no plant will exceed 1.5 g/te by the end of 2007.

- (4) Mercury emissions data will be provided to the authorities with total transparency, including independent third-party auditing, on a plant-by-plant basis. Ironically this goes beyond what some governments have been willing to offer up to now, as there has been considerable reticence in some countries about revealing the performance of individual plants in international discussions.
- (5) Remaining mercury cellrooms will close or convert to non-mercury processes when they reach the end of their economic lives. The exact date will depend on the availability of capital and on macroeconomic factors more under the control of governments than industry. All available independent analyses point to this equating to an end for the mercury process in Western Europe somewhere in the 2020s.
- (6) Mercury arising on shutdown will be disposed of in ways that do not increase emissions to the environment. Wastes will be handled, transported and disposed of using best environmental practice and best available techniques. The 12 000 tonnes of pure mercury from the cellrooms will be recycled. First preference will be re-use in remaining cellrooms to avoid any increase in the industry's mercury inventory. The remainder will so far as possible be returned to the mercury mines to displace tonne-for-tonne the need for mining and smelting new mercury which would otherwise increase the global anthropogenic inventory.

State of play

At the time of writing, much of this work is still ongoing and activity on the mercury issue within OSPAR is intense. The complexity of the issues is great, the stakes are high, and OSPAR has other important issues on its agenda. The best current estimate is that a revised version of PARCOM 90/3 will be approved by the Commission meeting in mid-2002 and that it will – unlike the original version – be binding and capable of implementation. But nothing is certain and it remains to be seen what kind of future OSPAR will choose for our industry – and perhaps for its own credibility!

2.5 Synthesis and solutions – learning points

This chapter has examined a major problem facing the chlor-alkali industry. It has been seen that the problem is no longer one of environmental pollution. Instead a conflict now exists between regulatory and political pressures deriving from some very negative perceptions of the chlor-alkali industry, and our continuing unwillingness to waste capital and skilled resources on accelerating a costly phase-out which is, in any case, going to occur over the next quarter century.

The solution comes in three parts.

- (1) The need to provide accurate, timely, transparent and credible information so that decision-makers at least have a factual basis from which to operate. Without a continuing commitment from industry to far greater transparency – especially in matters that are perceived as impinging on public or environmental health – our industry will be unsustainable. ‘Trust me – I’m a businessman’ works about as well as ‘Trust me – I’m a politician’. Even ‘Trust me – I’m a journalist’ works better!
- (2) The need to recognise that the issues will have to be resolved in a world where ‘perception is reality’ and regulations are driven more than by political pressure and public sentiment than by scientific reason, technological practicality or economic feasibility. Perception may not be the whole of reality, but if we deny that it has become an important aspect of reality we will not understand how to devise a sustainable future for ourselves.
- (3) The willingness to take actions that could not be justified solely on scientific, technological or economic grounds. There has been a paradigm shift. Science and technology are nowadays seen as just one way of looking at the world. Most of us in the chemical industry are trained to think logically. We should also remember that science does not deal in absolutes and is no more than a methodology for asking questions. If we have asked the right questions, the answers should generate *more* questions – that is how science progresses. But there are other ways of examining the world we live in – emotional, political and religious. Like science and technology, these approaches have their limitations but they are important to the achievement of the ‘triple bottom line’ of sustainable development that recognises economic, environmental and social inputs and outputs.

This chapter is presented unashamedly from a European perspective. It is after all in this continent that phrases like the ‘Precautionary Principle’ have gone beyond their existence as an ecological mantra and have become established as part of law-making. But let no one imagine for one moment that the problems and the challenges are unique to Europe or that they could be confined safely within its boundaries.

Environmentalism is international, our industry is world-wide, and our markets are global. The principle of the ‘global village’ applies. In the 1970s the USA led the environmental movement and US negotiators pressured the Europeans in international negotiations. By the 1990s the role reversal was complete and American pragmatists resisted European ‘greenery’ in government negotiations – and to some extent even within industry. We are already seeing in the negotiation of global environmental agreements attempts by European government negotiators to impose their interpretations of the ‘Precautionary Principle’ and the ‘Elimination Objective’ on the governments of North America and the Pacific Rim. The recent heated debate

in Bonn on the proposed UNEP Convention on Persistent Organic Pollutants is a case in point. When government negotiators state that 'elimination does not mean zero' and that '2020 is meant to indicate the date at which parallel lines meet' what hope is there for their credibility or our understanding?

But there has to be a growing convergence. It will be necessary to bring to bear on these problems a unique and challenging combination of pragmatism, business acumen and a respect for the intangible aspects of life. I am certain only of one thing: whatever the solutions to our problems – real or perceived – may be, they will be found not through the secrecy and confrontation of the past but through the dialogue and co-operation which we must find in the third millennium.

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Chapter 3

Euro Chlor Risk Assessment for the Marine Environment

V Garny

3.1 Introduction

While participating in the European Union programme on risk assessment of existing chemicals, Euro Chlor (representing all major European chlorine producers), recognised the need to carry out a detailed risk evaluation on chemicals linked to the production of chlorine. In view of concerns about specific risks of organohalogen compounds to the marine environment as a sink for all watercourses, Euro Chlor focused on this environmental compartment, with emphasis on the North Sea. This sea area has been extensively studied and is controlled by the Oslo and Paris Convention for the Prevention of Marine Pollution (OSPARCOM). For a series of chemicals on lists of concern adopted by the North Sea Conference (1990), risk assessments are being carried out to demonstrate their variable environmental profiles.

3.2 Principles

This voluntary risk assessment programme started in 1995 and concerned a list of 25 chemicals: dichloromethane, chloroform, tetrachloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, vinyl chloride, trichloroethene, tetrachloroethene, hexachlorobutadiene, monochlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, tetrachlorobenzene, hexachlorobenzene, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, pentachlorophenol, hexachlorocyclohexane, dioxins, PCB, DDT, and elemental mercury.

This chapter uses the formal EU risk assessment methodology laid down in the European Commission Regulation (1488/94) and follows closely the principles of the technical Guidance Document [1] of the Existing Substances Regulation (793/93).

The method compares the predicted environmental concentrations (PECs), as indices of exposure, with predicted no effect concentrations (PNECs), as indices of

effects. It comprises the collection and evaluation of data on environmental concentrations and effects on aquatic organisms. Basically the exposure data are retrieved from analytical programmes and effect data are derived from laboratory toxicity tests and/or field studies in both fresh- and marine-water organisms.

In addition, for substances with low water solubility and high lipophilicity the risks to be considered are those associated with potential to bioconcentrate in marine organisms, to partition to sediment and to biomagnify in the food chain.

Therefore, additional evaluations of effects on sediment organisms and fish predators were performed. In this respect, the method by Nendza *et al.* [2] was particularly useful as it describes the potential for secondary poisoning and magnification in marine organisms.

3.3 Methods

3.3.1 Exposure assessment

For most of the compounds considered, their environmental presence may not only result from direct release during present production or use but also from historical production and use, natural formation or transformation of other products. Therefore, to derive predicted environmental concentrations (PECs), data collected during analytical monitoring programmes are preferred to modelling data provided they are reliable and representative [1].

For the exposure assessment, monitoring data for larger rivers and estuaries as well as coastal areas were collected with focus on the North Sea. These data represent worst-case situations as additional dilution in the sea will take place. Because reliability and representativity of these monitoring values were not checked in detail, they have been used representing both typical, and worst-case scenarios. Generally, it is not specified in the literature if sampling locations are close to a source of emission. Therefore, it has been assumed that the mean lower levels correspond to background regional concentrations while higher levels correspond to contaminated areas, or local sources. The latter scenario is considered as a worst case.

For some chemicals a large database was available that allows statistical evaluation. In such cases, mean values were considered as typical PECs and the 90th percentile as a worst-case scenario.

Data collected from biota were used to estimate the critical body burden of fish-eating predators.

3.3.2 Effect assessment

For the effect assessment, the following three taxonomic groups representing three trophic levels have been considered: fish, invertebrates and aquatic plants. The

evaluation of the quality of the available ecotoxicological data was completed according to criteria described in the TGD [1].

In general, only valid studies were used to derive predicted no effect concentrations (PNECs). Because in some cases only a few valid data were available, studies ‘valid with restrictions’ have been used based on expert judgement. Invalid or non-assignable studies have not been used. In instances of volatile compounds, valid studies were generally those using closed, flow-through systems, preferably with analytical measurements.

Also, in order to increase the confidence of the PNEC value, both marine and freshwater data have been used to identify the most sensitive species. For the evaluated compounds, no significant differences in the sensitivity of marine versus freshwater organisms were observed.

3.3.3 Risk assessment

The risk evaluation involves comparing the predicted environmental concentrations (PECs) with the predicted no effect concentrations (PNECs) and is expressed as a hazard quotient for the aquatic environment (Table 3.1). This quotient will indicate the necessity for further refinement of the risk assessment or eventually for risk reduction.

Table 3.1 Results of PEC/PNEC evaluation of various chlorinated chemicals: aquatic compartment.

Chemical	PEC (typical, estuary)	PNEC (aquatic)	PEC/PNEC
Chloroform	0.2 µg l ⁻¹	1-72 µg l ⁻¹	0.0028-0.2
1,2-Dichloroethane	0.5 µg l ⁻¹	1100 µg l ⁻¹	0.00045
1,1,2-Trichloroethane	0.01 µg l ⁻¹	300 µg l ⁻¹	0.000033
Trichloroethene	0.1 µg l ⁻¹	150 µg l ⁻¹	0.00067
Tetrachloroethene	0.2 µg l ⁻¹	51 µg l ⁻¹	0.004
1,1,1-Trichloroethane	0.024 µg l ⁻¹	21 µg l ⁻¹	0.001
Carbon tetrachloride	0.003 µg l ⁻¹	7 µg l ⁻¹	0.0004
Dichloromethane	<0.1 µg l ⁻¹	830 µg l ⁻¹	<0.00012
Vinyl chloride	0.15 µg l ⁻¹ (worst case)	210 µg l ⁻¹	0.0007
Monochlorobenzene	<0.005 µg l ⁻¹ (estimated)	32 µg l ⁻¹	<0.002
1,2-Dichlorobenzene	<0.1 µg l ⁻¹	37 µg l ⁻¹	<0.003
1,4-Dichlorobenzene	<0.1 µg l ⁻¹	20 µg l ⁻¹	<0.005
1,2,4-Trichlorobenzene	<0.01 µg l ⁻¹	4 µg l ⁻¹	<0.0025
Pentachlorophenol	0.007 µg l ⁻¹	1 µg l ⁻¹	0.07
Mercury	170 ng l ⁻¹	470 ng l ⁻¹	0.36

The risk posed by the potential to concentrate into sediments was approached similarly to the aquatic compartment, i.e. using a PEC/PNEC ratio (Table 3.2). When no actual effect data on sediment organisms were available, PNECs in sediments were estimated on the basis of physico-chemical parameters and PNECs in water [1]. The risk posed by the potential to bioconcentrate in fish was assessed by the methodology described by Nendza *et al.* [2] with the determination of the critical body burden (CBB). This parameter predicts the level of the chemical in the organism which could

Table 3.2 Results of PEC/PNEC evaluation of PCP and mercury: sediments.

Chemicals	PEC (worst case, estuary)	PNEC (sediment)	PEC/PNEC
Pentachlorophenol	$< 10 \mu\text{g kg}^{-1}$	$62 \mu\text{g kg}^{-1}$	< 0.16
Mercury	1.6 mg kg^{-1}	32.2 mg kg^{-1}	0.05

entail the first toxic effect. This level is then compared with monitoring data in marine fish.

The risk posed to predators eating contaminated fish is determined by comparing the estimated daily intake (EDI) of fish predators (birds or mammals) with the predicted no-effect concentration in these predatory species. If adequate data are missing, the latter value was estimated from laboratory rodent or meat-eating animals (Table 3.3).

Table 3.3 Results of EDI/PNEC evaluations of HCB and mercury: predators.

Chemicals	EDI (marine fish)	PNEC (predators)	EDI/PNEC
Hexachlorobenzene	$0.33\text{--}0.45 \mu\text{g kg}^{-1} \text{ bw}^a$	$0.4 \mu\text{g kg}^{-1} \text{ bw day}^{-1}$ (mink)	0.825–1.13
Mercury	$12 \mu\text{g kg}^{-1} \text{ bw}$	$18 \mu\text{g kg}^{-1} \text{ bw day}^{-1}$ (mink)	0.7

^a Denotes body weight.

This risk assessment is not intended to cover accidents or effects of mixtures.

3.3.4 Dioxins, PCBs and DDT

Dioxins are formed as unwanted contaminants in a variety of combustion and manufacturing processes as well as through natural processes. The European Dioxin Inventory 1993–1995 showed that the contribution from the chemical industry was less than 1% of total dioxin emissions.

Despite the minor contribution from the chemical industry Euro Chlor actively participates in minimising the dioxin emissions by promoting and applying Best Available Techniques. Euro Chlor also assists in the collection of monitoring data to follow dioxin trends in the environment.

No Euro Chlor member manufactures PCBs. Euro Chlor supports restrictions on production and use of PCBs world-wide. Euro Chlor believes that the rapid destruction of withdrawn PCBs should be mandatory and is ready to assist in the destruction programmes of PCBs by providing the appropriate incineration facilities.

No Euro Chlor member manufactures DDT and the organisation supports use restriction approaches on DDT.

3.4 Conclusion

The chlorinated chemicals assessed do not have the same risk profile. For the more volatile chemicals the safety margins between the actual exposure and the level at which no effect on the environment would be expected is quite high. For more persistent chemicals there is a need to look to the environmental compartment where they can be accumulated (mainly in sediments and biota). For some of these chemicals the safety margin is quite low and in worst-case situations serious effects may occur. For the very persistent, bioaccumulative and toxic chemicals (like dioxins, PCBs and DDT), acceptable environmental concentrations are so low and difficult to control that the industry is committed to reducing as far as possible releases to the environment through application of Best Available Techniques (BAT), mainly with respect to dioxins. For other chemicals (PCBs, DDT), production has already been halted for some years.

Acknowledgements

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Chapter 4

Chlorine Production with Oxygen-depolarised Cathodes on an Industrial Scale

F Gestermann and A Ottaviani

4.1 Introduction

Encouraging laboratory experiments since 1994 with oxygen-depolarised cathodes (ODC) in chlor-alkali as well as hydrochloric acid electrolysis motivated the development of this technique up to the industrial scale. Based on the predictions of the theory, the reduction of cell voltage could be expected up to 1 V (Fig. 4.1) for both applications. Early on, the proper choice and improvement of ODC, deriving mainly from the DeNora group, led to results with voltages as predicted in short tests as well as in endurance tests conducted over dozens of months at the Bayer endurance test facilities.

The two types of electrolysis differ specifically in their elementary processes which led to different cell concepts.

4.2 NaCl electrolysis with ODC

For the NaCl electrolysis, finite-gap operation proved initially to be the most promising way to realise good and reproducible cell voltages. Predominantly the reasons were a proper control of the membrane water content, the relatively simple retrofit of existing membrane electrolyzers and the ongoing utilisation of the peripheral caustic equipment with the ODC technique.

The main problem, the height-dependent differential pressure between the catholyte gap and oxygen across the ODC, could be solved with the pressure compensation system based on oxygen supply via gas pockets [1] (see Fig. 4.2). The first successful piloting was done in October 1995 on the basis of Bayer engineering and construction. In a four-gas-pocket element with each electrode segment of $180 \times 180 \text{ mm}^2$ individually supplied with power, the proper function of pressure compensation could be proven for a total height of 90 cm.

This was the basis of the co-operation between Bayer and DeNora with the goal

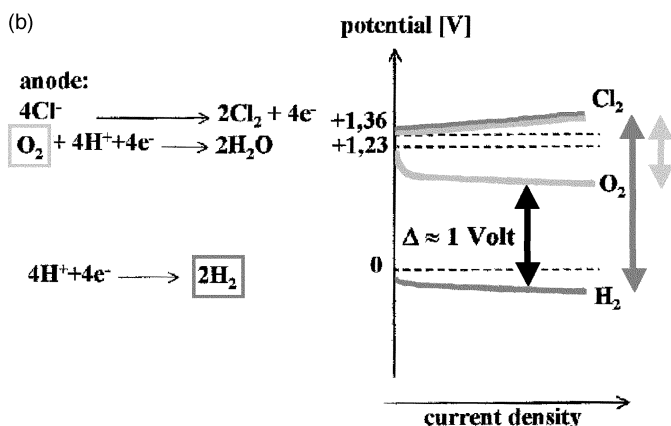
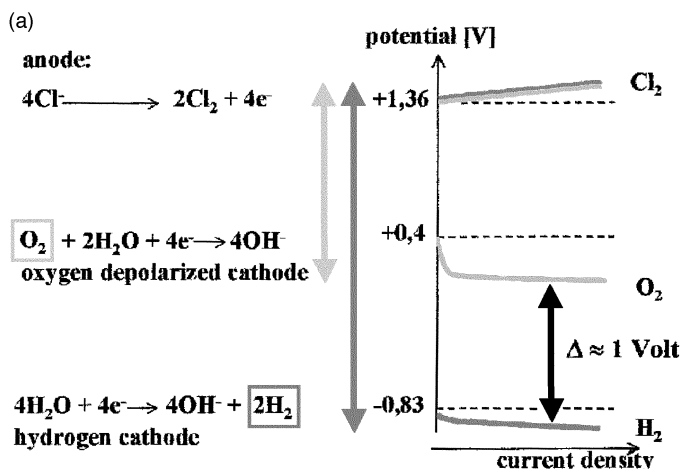


Fig. 4.1 (a) Chlor-alkali electrode potentials: oxygen reduction versus hydrogen production. (b) HCl electrode potentials: oxygen reduction versus hydrogen production.

being to develop an electrolyser capable of exploiting the ODC technique on an industrial scale. The commonly developed cell concept utilising vented gas pockets in a cascade-type oxygen supply [2] was successfully piloted in a four-element bipolar electrolyser of full industrial dimensions. The test runs in the Bayer endurance test facility (Fig 4.3) began in August 1997 and the results were more than encouraging, as shown in Fig. 4.4, although considerable technical detail still had to be resolved on the way to the full technical dimension. For an element height of 120 cm and an element size of 0.25 m^2 a power consumption of less than $1380 \text{ kWh tonne}^{-1} \text{ NaOH}$ under normalised conditions (3 kA m^{-2} , 90°C , 32% NaOH) could be established. Current densities up to 6 kA m^{-2} could be operated for a number of weeks and values up to 7 kA m^{-2} (the rectifier limit) were used in short-time runs.

The next step was the full industrial-size element. It was developed jointly by Bayer and DeNora and constructed at the DeNora production site in Milan. The result of numerous detailed solutions and innovations was a test electrolyser with

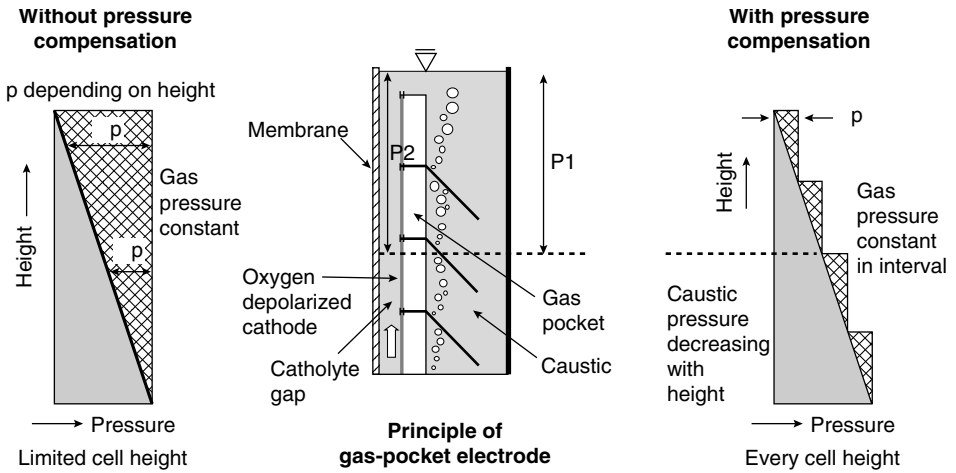


Fig. 4.2 The effect of pressure compensation in chlor-alkali electrolysis.

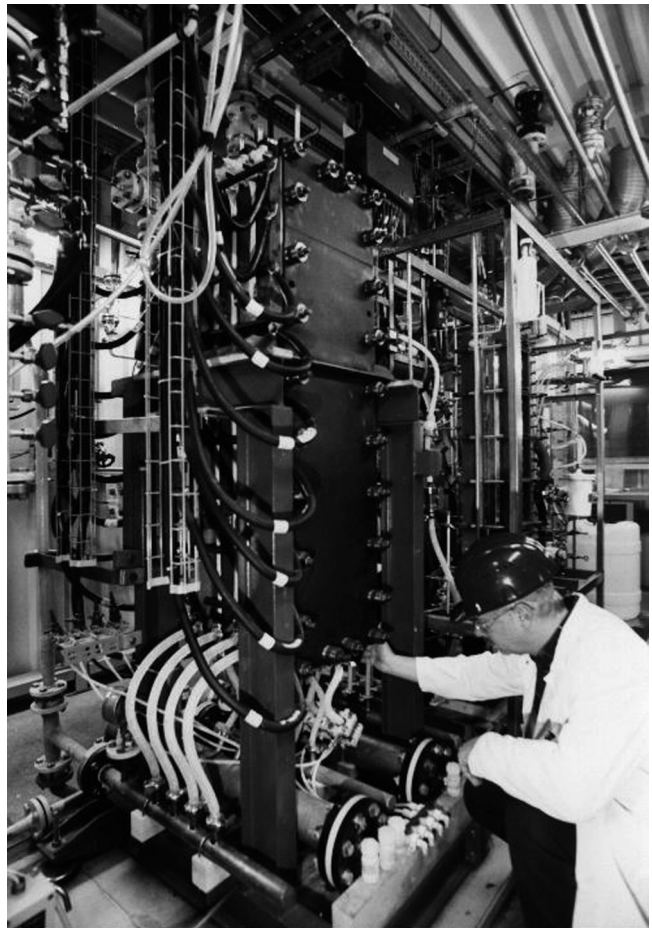


Fig. 4.3 The second pilot electrolyser plant based on a full technical operating height at the Bayer endurance test facility.

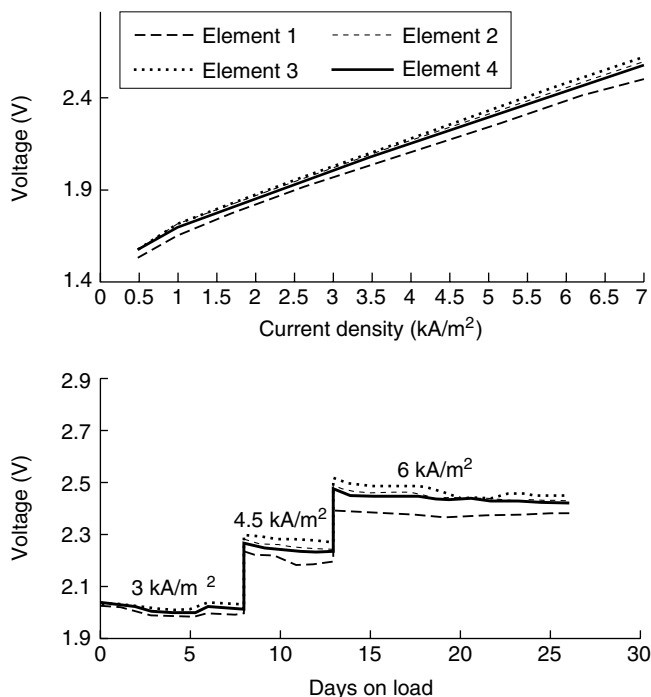


Fig. 4.4 Test results for the second pilot electrolyser: (a) development of cell voltage with increasing current density; (b) the first endurance test.

16 bipolar elements of area 2.5 m^2 each in a filter press arrangement (Fig 4.5). The first start-up in December 1998 at the Bayer membrane electrolyser test site in Leverkusen was a surprise. Despite the fact that this was a relatively unknown technique, and the first industrial-scale ODC electrolyser, the test plant was commissioned up to 3 kA m^{-2} within 2 h and remained operational without problems from the electrolyser for quite a long period. The operational results proved the

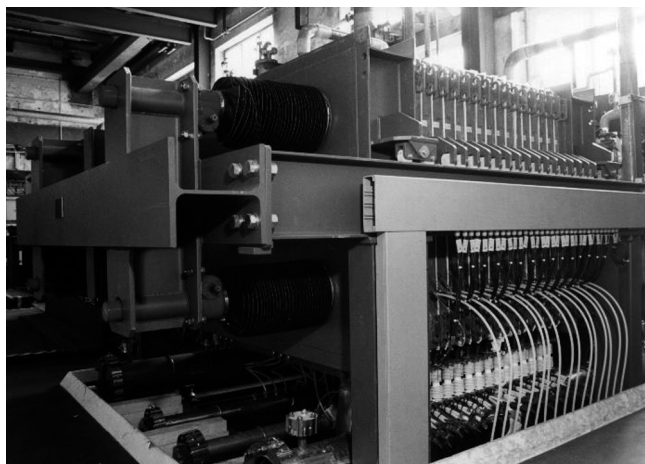


Fig. 4.5 The first industrial-scale test electrolyser at start-up on 3 December 1998.

feasibility and attractiveness of this technique. The results were comparable to the experience of the pilot-plant operation: the standardised power consumption at 3 kA m^{-2} again was less than $1400 \text{ kWh tonne}^{-1} \text{ NaOH}$ and the single-element voltages were spread below 100 mV .

Following successful testing of the bubble jet system [3] at pilot scale, the plant was scaled to full technical size (2.5 m^2 elements) and successfully tested. The anolyte flow-out of the elements showed a completely pulsation-free operation with all benefits for the membrane lifetime. Despite the rather good results of this first run a design review was started to improve the electrolyser element design.

Thus, after more than 180 days of operation, electrolyser and plant reconstruction began for a mixed-mode operation (ODC and H_2) to test the second generation of elements. The improved element design is now optimised for rationalised industrial manufacturing with a laser-welding technique, which will be performed in the DeNora (Germany) production site in Rodenbach near Frankfurt. The element design is also optimised for industrial-scale ODC insertion and re-electroding. The new element type basically has the same design for both types of operation. In a simple procedure, the ODC technique can be used in the form of a fully pre-manufactured gas-pocket unit with all hydraulic details as well as a hydrogen cathode. The design allows an easy retrofittability between ODC and standard electrolysis.

In the same procedure, electrolyser elements capable of ODC operation as well as elements in the hydrogen mode are tested in parallel. As a supplementary effect it was seen that the performance of the element (which in the anode half-cell was optimised for the special demands of the thermohydraulics of finite-gap ODC operation) demonstrated excellent operational results. The standardised power consumption of 4 kA m^{-2} remains below $2050 \text{ kWh tonne}^{-1} \text{ NaOH}$ even after several months of operation.

A demonstration of the ODC technique in a full-scale industrial electrolyser with more than 70 elements is in preparation.

4.3 HCl electrolysis with ODC

For HCl electrolysis the cathodic reaction product is water, which is easily drained through the ODC without affecting the membrane water content. Consequently, the ODC can be attached directly to the membrane and pressure compensation is not necessary. The cell concept, which was developed in another co-operation with DeNora, could not be simpler – the basic cell principle is shown in Fig. 4.6. Initial laboratory tests conducted in 1994 at Bayer on the basis of old GE developments [4] demonstrated the feasibility of HCl electrolysis with ODC and the potential for a reduction of the cell voltage to about one-third of present values.

Very early on the decision was made that an electrolyser with this ODC technique

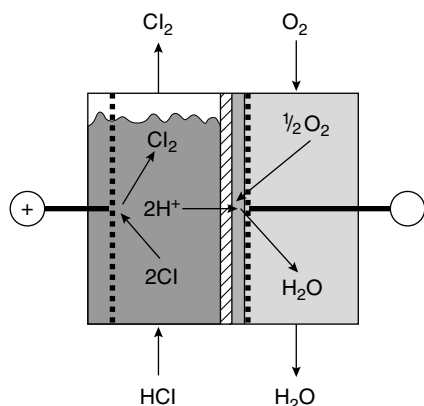


Fig. 4.6 The method of HCl electrolysis with oxygen-depolarised cathodes (ODC).

should be metallic and similar to the set-up of the chlor-alkali technique. To simplify the electrical contact of the ODC, it is pressed against the membrane of the current distributor on the cathode side via hydrostatic pressure from the anode side. A first pilot study was started in February 1997 at the Bayer test site with a four-bipolar-element electrolyser of full technical height and 0.85 m^2 element area in a filter press arrangement (Fig. 4.7). Since then, it has been successfully operated and has two-fold proved the feasibility of the new ODC technique using purely metallic elements manufactured from TiPd alloy [5].

Owing to the fact that nearly all the heat generated by this type of electrolyser has to be dissipated via the anolyte flow, for the full industrial-scale demonstration electrolyser with an element size 2.5 m^2 it was decided to use the bubble jet system [3], which was successfully tested previously with the chlor-alkali method. For HCl electrolysis, which from the material side is optimised to an approximate operation temperature of 60°C , an intense vertical temperature-profile flattening is essential to reduce the external flow rates and to allow rather low anode-side inlet temperatures. The intensive vertical mixing with the bubble jet proved to be suitable for this purpose.

On this basis a demonstration plant having a capacity of $10\,000 \text{ tonnes a}^{-1}$ of chlorine was built in the Bayer production plant at Leverkusen. The plant was successfully commissioned on 4 January 2000. Figure 4.8 illustrates the electrolyser section of the plant, with the peripheral apparatus arranged mostly outside this building. The 76-element electrolyser was found to behave very smoothly and could be immediately operated up to 5 kA m^{-2} without any problems. Permanent operation is performed at 4 kA m^{-2} . The power consumption was found to be about $1080 \text{ kWh tonne}^{-1} \text{ Cl}_2$ with a typical current efficiency of nearly 100%. Chlorine purity is found to be 99.9%, which obviates the need for a chlorine liquefaction purification and therefore simplifies the plant drastically.

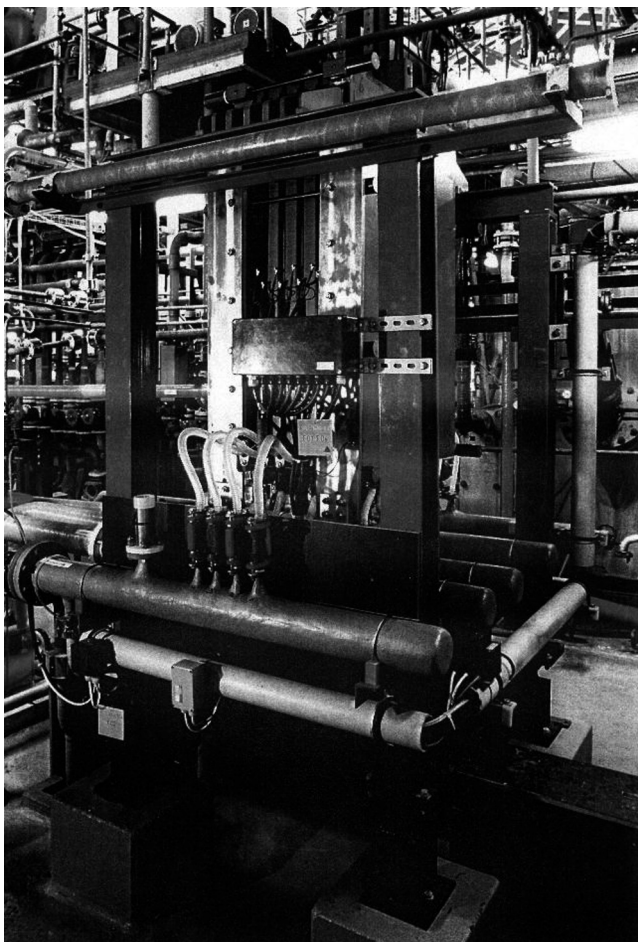


Fig. 4.7 The pilot electrolyser for HCl electrolysis with ODC.

Improved next-generation ODC with a catalyst based on rhodium [6] promises an even more simplified plant concept. This is due to the fact that this type of ODC does not require polarisation during shut-down as an inert cathode is no longer necessary. The plant can simply be put at stand-by where the anode side, as well as the HCl circuit, remains pressurised under chlorine saturation. Therefore, re-starting the operation is very simple and the chlorine supply is derived directly from the electrolysis and liquid chlorine evaporation is no longer necessary. Instead, with a liquid chlorine buffer, the system can be re-started from the hydrochloric acid storage tank.

With these improvements, this type of HCl electrolysis plant becomes increasingly simplified and will thus provide a near-ideal tool for HCl recycling.



Fig. 4.8 The demonstration plant for HCl electrolysis with ODC at start-up on 4 January 2000.

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Chapter 5

Deactivation of Thermally Formed $\text{RuO}_2 + \text{TiO}_2$ Coatings During Chlorine Evolution: Mechanisms and Reactivation Measures

T V Bommaraju, C-P Chen and V I Birss

5.1 Introduction

Ru/Ti oxide anodes, formed by thermal decomposition techniques on titanium substrates and used in the chlor-alkali industry, typically contain >30 at.% RuO_2 , the remainder being TiO_2 [1, 2]. The Ru metal loading in these oxide mixtures is generally in the range of $4\text{--}10\text{ g m}^{-2}$, depending on whether their use is in diaphragm or in membrane (or chlorate) cells. Ru/Ti oxides of this composition exhibit chlorine overpotentials of $40\text{--}60\text{ mV}$ at current densities of $200\text{--}250\text{ mA cm}^{-2}$ in 5 M NaCl solutions at $80\text{--}90^\circ\text{C}$. However, with extended usage in electrolytic chlorine cells, in practice, the chlorine overpotential increases to $300\text{--}400\text{ mV}$, and the anode is considered to have become ‘deactivated’.

The escalation in the anode overpotential can be a consequence of:

- (1) a loss of active surface sites by blockage owing to insoluble surface layers (e.g. MnO_2 , BaSO_4 , Fe oxides, etc.) or impurities (e.g. organics) in the solution;
- (2) a loss of Ru loading in the coating by erosion and/or corrosion;
- (3) the formation of an insulating TiO_2 layer at the Ti substrate/coating interface; and/or
- (4) the surface depletion of RuO_2 (via the loss of Ru-based adsorbed intermediates, which are crucial to the chlorine and oxygen evolution reactions).

Anode deactivation via the pathways (1) and (2) is comprehensible. However, it is more difficult to explain the increased anode potential when the Ru loading is high, and when impurities are not present on the failed anode surfaces. Note that when the Ru loading is less than 2 g m^{-2} , and when the mole percentage RuO_2 is less than 20, the anode potential on freshly formed anodes is unacceptably high (Fig. 5.1). Also, a notable increase in the resistivity of mixed oxides of RuO_2 and TiO_2 was observed [3–7] when the RuO_2 content is substantially less than 20 at.% (Fig. 5.2).

The mechanisms involved in the deactivation of $\text{RuO}_2/\text{TiO}_2$ -based anodes during

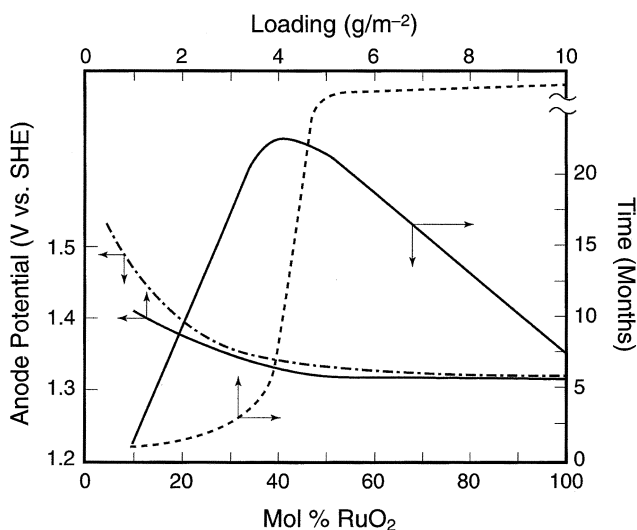


Fig. 5.1 Variation of the anode potential at 3.0 kA m^{-2} and the operating life with mol% RuO₂ and percentage loading for a 40 mol% RuO₂ electrode, plotted from the data in Ref. [18]. Operating life in accelerated testing was determined in 300 g l^{-1} at pH 2.0–2.5 and at 80°C .

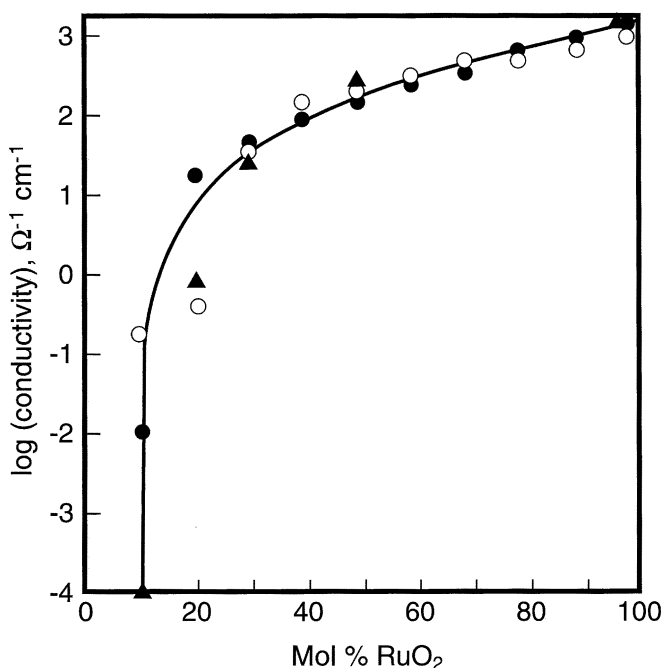


Fig. 5.2 Variation of conductivity with mol% RuO₂ in the coating. The measurement technique and the final firing temperatures are noted below. The symbols are: ● = 350–600°C/ direct resistance measurement (Ref. [3]); ○ = 450°C/a.c. impedance (Ref. [4]); ▲ = 400°C/ direct resistivity measurement (Ref. [5]).

the course of the chlorine and oxygen evolution reactions have been the subject of several recent reviews [1, 2, 8], and various publications [9–29]. It is unequivocally agreed that, during electrolysis, some RuO₂ does dissolve electrochemically (although the magnitude of the rate of dissolution is not known with certainty), and that some is also lost by erosion [9, 11]. The corrosion rate of RuO₂ is minimal around pH 1–2 [17, 21] and increases below a pH of approximately 0.2 (forming RuOHCl₅²⁻) [17],

and above a pH of approximately 4 (forming RuO_4^{-2} and gaseous RuO_4) [12, 13, 24, 30]. The RuO_2 dissolution rate increases with:

- (1) increasing current density [12, 14];
- (2) increasing percentage O_2 generation [10, 23, 24];
- (3) decreasing NaCl concentration [16, 26]; and
- (4) an increasing number of shut-downs of operating cells [12, 22].

TiO_2 dissolution is believed to be chemical [20], resulting in the formation of TiO^{2+} . It is well acknowledged that RuO_2 anodes dissolve during operation in NaCl and H_2SO_4 solutions. However, the mechanism of deactivation of the Ru/Ti oxide anodes has been attributed by some [14, 17, 25, 28, 31] to the surface depletion of RuO_2 , resulting in the development of a high resistivity $\text{RuO}_2 + \text{TiO}_2$ composition when the RuO_2 content is much less than 20 at.%. Others [13–15, 29] have attributed anode failure to the build-up of a TiO_2 layer at the Ti substrate/coating interface, for which direct evidence is lacking.

The purpose of this chapter is to provide an understanding of the causal factors leading to these high anode overpotentials. In addition, the objectives are to discover preventative measures to extend the operating life of these anodes, and to develop rejuvenation procedures, which could serve to reactivate a failed anode that has a more than adequate loading of Ru in the coating. To meet these goals, the electrochemical behaviour of Ru/Ti oxides containing varying amounts of Ru was established by determining the chlorine evolution Tafel slopes, as well as the cyclic voltammetric and a.c. impedance response in chlorine-free solutions, during the process of deactivation. It is shown that the deactivated 40 at.% Ru electrodes behave like freshly formed Ru/Ti oxide electrodes containing small amounts of RuO_2 (<5 at.%), suggesting the depletion of RuO_2 from the outer region of the surface to be responsible for the high anode potentials following the deactivation of the electrodes. These studies were complemented by surface characterisation studies using secondary ion mass spectrometry (SIMS) with new and failed anodes from commercial operations.

5.2 Experimental

5.2.1 Electrodes for cyclic voltammetry (CV) and a.c. impedance experiments

The working electrodes (WEs) used in the CV and a.c. impedance experiments consisted of Ti wire substrates (99.99%, Johnson–Matthey, Inc., 2 mm diameter). The cross-sectional end of each bare Ti wire (0.0314 cm^2) was polished with 600 grit paper, rinsed with acetone, dried, rinsed with methylene chloride, dried again and then rinsed with triply distilled water before oxide-coating deposition.

Ru(III) chloride (18.2 g, Johnson–Matthey, Mallory Ltd.), Ti(IV) butoxide (45 ml, Aldrich) and 37% HCl (6 ml) were mixed together to make the coating solution. The Ti electrodes were dipped into this solution and allowed to air-dry and then heated at about $5^{\circ}\text{C min}^{-1}$ to 100°C , remaining at this temperature for 15 min to remove the solvent. The temperature was then increased at $10^{\circ}\text{C min}^{-1}$ to 440°C in air and maintained at 440°C for 30 min to decompose the Ru/Ti compounds, thus forming the mixed Ru/Ti oxides. Subsequently, the length of the oxide-coated Ti wire was wrapped in Teflon® tape, leaving only the cross-sectional end as the WE for immersion in solution.

The counter-electrode (CE) was a 40 at.% RuO_2 (the remainder being Ti oxide) electrode, having more than 100 times the apparent surface area of the WE. It was positioned inside a Teflon® tube to minimise the amount of hydrogen gas that could be released into the cell solution. An Ag/AgCl electrode was employed as the reference electrode (RE) at high temperatures, while a saturated calomel electrode (SCE) generally served as the RE at room temperature.

5.2.2 Equipment

An EG&G PARC 273 Potentiostat/Galvanostat was used in both the electrolysis and the CV experiments, coupled with an HP 7044B X/Y recorder. A Solartron 1255 HF Frequency Response Analyzer and a Solartron 1286 Electrochemical Interface were employed for the a.c. impedance measurements, using frequencies from 0.1 to 65 kHz and a 10 mV a.c. amplitude (effective) at either the open circuit potential (OCP) or at various applied potentials. As the RE can introduce a time delay at high frequencies, observed as a phase shift owing to its resistance and capacitance characteristics, an additional Pt wire electrode was placed in the cell and was connected via a $6.8\ \mu\text{F}$ capacitor to the RE lead [32–34].

5.2.3 Solutions and general experimental conditions

The solution used for all experimentation was 5 M NaCl, made up using triply distilled water. Electrolysis experiments were carried out in a one-compartment cell at either room temperature or at 90°C . All electrochemical experiments were carried out using a two-compartment cell, with the RE compartment connected to the WE and CE compartments via a Luggin capillary.

5.2.4 Ru/Ti oxide deactivation procedures

As anode deactivation by the application of a constant anodic current density of between 200 and $250\ \text{mA cm}^{-2}$ in 5 M NaCl (pH maintained at 3–5) was found to require many days, it was found to be more effective to deactivate the anodes in an acidified salt solution (5 M NaCl + 0.1 M HCl). This was performed either by

applying a constant anodic current density, by square-wave current cycling (from $+320$ to -130 mA cm^{-2} , 30 s for each pulse), by overpotential cycling (100 mV s^{-1}) between *c.* $+1 \text{ V}$ and *c.* -0.5 V versus the OCP, or by applying square-wave (30 s) potential cycles (1.35 to -0.3 V versus SCE).

5.2.5 Surface characterisation studies

Secondary ion mass spectrometry (SIMS) was used to characterise the coatings for their Ti, Ru and O stoichiometry on the surface and as a function of depth into the coating. A PHI 6650 Quadrupole mass spectrometer, with Cs^+ as the ion source was used in these studies. The conversion of the measured secondary ion counts to concentration was performed using relative sensitivity factors, which were first determined with a standard sample containing known amounts of RuO_2 and TiO_2 . All of the SIMS profiles were repeated several times, to determine the measurement precision, which was typically $\pm 10\%$.

5.3 Results and discussion

5.3.1 Electrochemical characterisation studies

Anodic polarisation behaviour of fresh and deactivated Ru/Ti oxide electrodes during chlorine evolution

The time dependence of the chlorine overpotential (measured intermittently at 230 mA cm^{-2}), observed when a $40 \text{ at.}\%$ Ru electrode was subjected to overpotential cycling in the range of 900 to -600 mV in 5 M NaCl at 90°C , shows the overpotential to increase from an initial value of *c.* 70 mV (often lower values of *c.* 40 mV are seen) to more than 400 mV , indicating that, with time, the chlorine evolution reaction is occurring on an increasingly poorly conducting surface film. Similar deactivation phenomena were also observed by using square-wave current cycling from 320 mA cm^{-2} to -130 mA cm^{-2} (30 s pulse duration) in $5 \text{ M NaCl} + 0.1 \text{ M HCl}$ solutions at 90°C .

Figure 5.3 depicts the current–voltage behaviour of 5 – $40 \text{ at.}\%$ Ru/Ti oxide electrodes prior to deactivation at room temperature. These plots show, as observed previously [18, 35], increasing Tafel slopes (*b*) and a decrease in the exchange current density, i_0 , values for the chlorine evolution reaction as the Ru content of the oxide coating is lowered. The Tafel slope is *c.* 30 – 40 mV for the 30 – $40 \text{ at.}\%$ Ru electrodes, while for the $5 \text{ at.}\%$ Ru oxide, it has increased to *c.* 130 mV . The decreasing i_0 for the chlorine evolution reaction with decreasing *at.}\% Ru reflects a decreasing number of active Ru sites with the decreasing *at.}\% Ru. In contrast, the increasing Tafel slope with decreasing *at.}\% Ru can arise for two possible reasons. Acknowledging that the***

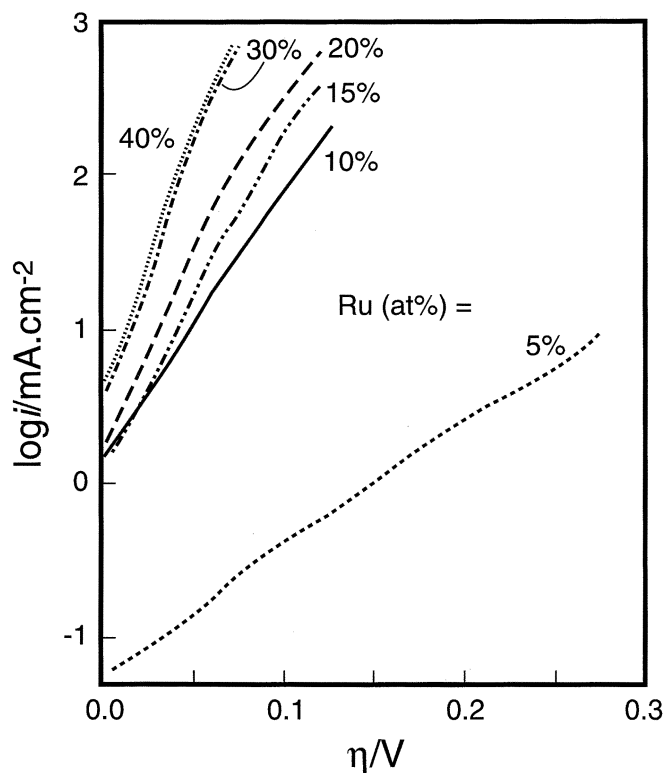


Fig. 5.3 Effect of Ru content on Tafel plot of fresh Ru/Ti oxide electrodes in 5 M NaCl (pH of approximately 3.5) at room temperature (with IR compensation).

Tafel slope for the chlorine evolution reaction follows an electrochemical desorption-type mechanism, it can be expressed [36, 37] in terms of the electrode surface coverage by the adsorbed Cl intermediates, θ_{ad} , as:

$$b = \frac{RT}{F(1.5 - \theta_{ad})} \quad (5.1)$$

At low coverage, the Tafel slope will be $2RT/3F$ or *c.* 40 mV, as observed on high at.% Ru electrodes. As the at.% Ru decreases, the number of Ru sites decrease, resulting in more coverage of the active Ru sites by θ_{ad} . Hence θ_{ad} will approach 1 and the Tafel slope will tend to reach values of $2RT/F$ or 120 mV, thus potentially explaining the results in Fig. 5.3. Alternatively, this change in the Tafel slope may arise from an increase in the electrical resistivity of the low at.% Ru electrodes, during the course of the chlorine evolution reaction [35].

Current–voltage profiles for chlorine evolution, obtained at various times between periods of square-wave potential cycling (1.35 to -0.32 V versus SCE, 60 s cycle⁻¹), all at the same 40 at.% Ru electrode, are shown in Fig. 5.4. It can be seen that the activity of these electrodes increases at the beginning of the deactivation period, as revealed by the decrease in the overpotential at approximately 5 h. This may arise, at least in part, from

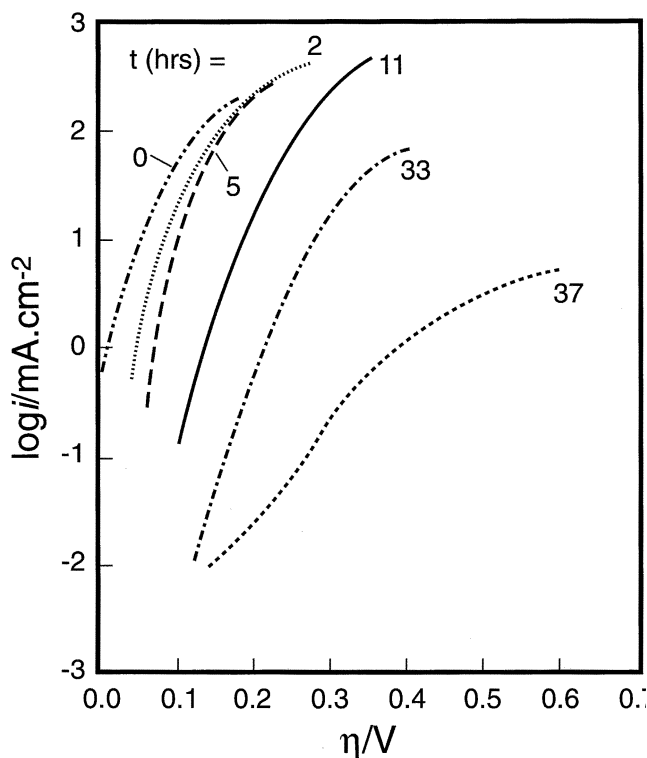


Fig. 5.4 Time dependence of i/E profiles during chlorine evolution at a 40 at.% Ru electrode in 5 M NaCl + 0.1 M HCl at room temperature (without IR compensation), subjected to square-wave potential cycling (from 1.35 to -0.32 V versus SCE at 60 s cycle^{-1}). The numbers in the figure refer to the time of electrolysis in hours. Each Tafel plot is shifted to the right by 20 mV to avoid overlapping.

an increased surface area of the electrode during these initial stages, as loosely attached oxide particles are lost from the surface. Subsequent profiles show a slowly increasing Tafel slope and a decreasing i_0 value with increasing time of electrolysis. At between 33 and 37 h of electrolysis, a sharp increase in the b value is seen, to $c.$ 150 mV.

A comparison of the data in Figs 5.3 and 5.4 shows that a 40 at.% Ru electrode behaves like low at.% Ru electrodes, after the anode is subjected to long periods of potential or current cycling. This strongly suggests that Ru dissolution is occurring from the coating in the present series of experiments.

It should be pointed out that the changes in the Tafel slope are not only a function of at.% Ru, but also a result of decreased RuO_2 loading [18], as shown in Fig. 5.5. The increasing anode potential with decreasing RuO_2 loading (at a constant at.% RuO_2) is a consequence of the altered chlorine evolution mechanism. Also, the reduction in anode life with low initial loading arises from the lack of compactness of the coating in the thin layers. As a result, the Ti substrate can develop a TiO_2 layer, contributing to the increased anode potential.

Cyclic voltammetry (CV) of fresh and deactivated electrodes

The CV features (Fig. 5.6) of the 40 at.% Ru/Ti oxide electrodes before, during and after deactivation (achieved by current pulsing between 0 and 0.955 A cm^{-2}) were

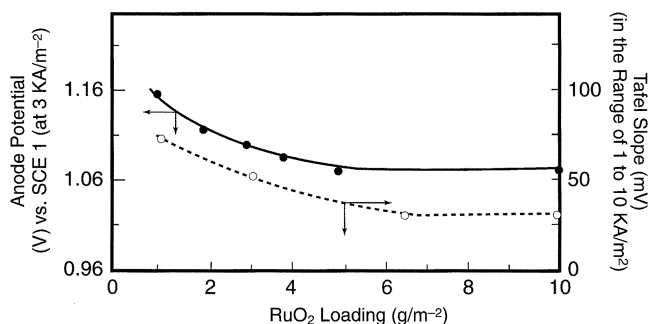


Fig. 5.5 Variation of the Tafel slope and the anode potential with RuO_2 loading (plotted from the data in Ref. [18]).

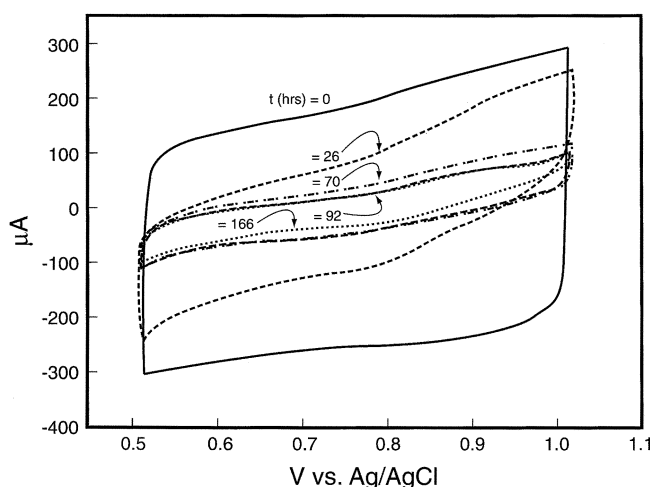


Fig. 5.6 Cyclic voltammetry of a 40 at.% Ru electrode in 5 M NaCl (pH of approximately 3.50) at various times during potential cycling.

monitored from 0.5 to 1.0 V versus SCE at 100 mV s^{-1} in fresh 5 M NaCl solution (pH 3–5) at 90°C . These potential limits were chosen to avoid any Faradaic interference due to the occurrence of chlorine, oxygen and hydrogen evolution/reduction reactions.

It was found that the fresh electrode gave the typical pseudocapacitive response of Ru oxide [37, 38], changing reversibly when the direction of potential cycling is changed. A decrease of up to a factor of 10 was observed in the response after approximately 70 h of deactivation. The CV response of fresh electrodes of various Ru contents at 90°C is shown in Fig. 5.7, for comparison. Consistent with the literature [18], the pseudocapacitive response decreases sharply when the RuO_2 content of the oxide is below *c.* 10 at.%, and there are no significant differences in the response of electrodes containing 20–40 at.% Ru. By comparing the CV response of fresh electrodes of relatively low Ru content with the response of the 40 at.% Ru electrode after long periods of electrolysis, there is again strong evidence that the Ru concentration decreases substantially with time of electrolysis. This may occur either only at the oxide surface or throughout its bulk.

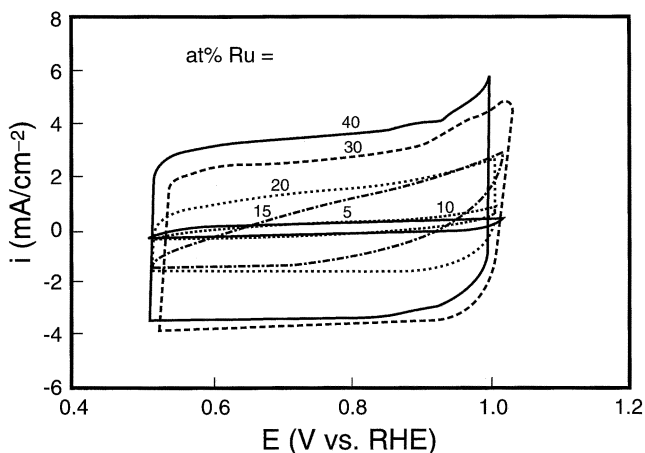


Fig. 5.7 Cyclic voltammetry of fresh Ru/Ti oxide electrodes with different Ru content of 2 μm thickness in 5 M NaCl (pH of approximately 3.5) at 100 mV s^{-1} at 90°C.

A.C. impedance behaviour of fresh and deactivated Ru/Ti oxide electrodes

To further understand and characterise the oxide deactivation process, a.c. impedance studies were carried out, primarily with a 30 at.% Ru/Ti electrode, at various stages during deactivation. These data were compared to those obtained for freshly formed Ru/Ti oxide films, ranging in Ru content from 5 to 40 at.%. Impedance data were collected at the oxide OCP (approximately 0.9 V versus SCE) in fresh NaCl solutions. Under these conditions, no chlorine reactions can occur and the OCP is defined by the equilibria of the redox states on the Ru oxide surface. Deactivation was generally accomplished by square-wave potential cycling, using overpotentials versus the chlorine/chloride potential of 1.59 to -0.08 V (60 s cycle^{-1}) in 5 M NaCl + 0.1 M HCl solutions at room temperature.

The impedance and phase-angle Bode plots, obtained during the course of deactivation of a 30 at.% Ru electrode, are presented in Fig. 5.8. For comparison, data [35] for freshly formed Ru/Ti oxide electrodes containing varying amounts of Ru are shown in Fig. 5.9. During the initial stages of deactivation, the phase-angle plot of the 30 at.% Ru electrode (Fig. 5.8) shows the close to ideal capacitive behaviour seen for freshly formed 30 or 40 at.% Ru electrodes (Fig. 5.9), as expected. However, after over one hour of deactivation, the phase-angle plots (Fig. 5.8) begin to reveal a peak in the high frequency range, and a phase-angle of $50\text{--}70^\circ$ develops at lower frequencies. The impedance increases significantly, as seen at low frequencies, from c. 10Ω to more than 500Ω after about 2 h of deactivation by potential cycling. A comparison of the results of Fig. 5.8 (after more than 1 h of deactivation of the 30 at.% Ru electrode) with those of Fig. 5.9 indicates clearly that the impedance response becomes increasingly similar to that of freshly prepared low at.% Ru oxide coatings.

It is well recognised [1, 36, 38, 39] that the electrochemical response (that is the a.c. impedance and cyclic voltammetry) of Ru/Ti oxides at the OCP is due to the pseudocapacitive reaction:

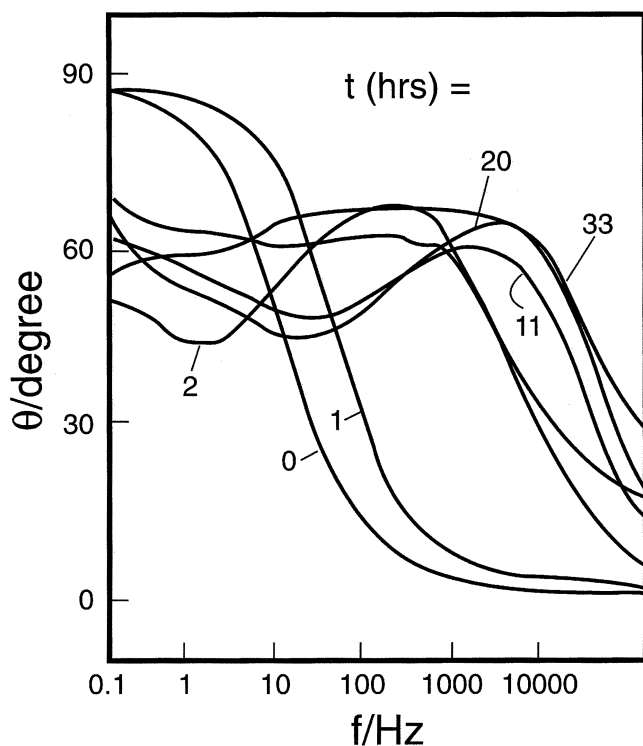
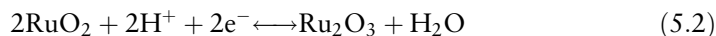


Fig. 5.8 Time dependence of impedance of 30 at.% Ru electrodes during deactivation in 5 M NaCl + 0.1 M HCl at room temperature. The electrodes were subjected to square-wave potential cycling from 1.35 to -0.32 V versus SCE at 60 s cycle^{-1} . Impedance was measured in 5 M NaCl at room temperature at OCP.



Theoretical investigations have shown [35, 39–44] that the a.c. impedance, $Z_p(p)$, associated with Equation 5.2, on a porous electrode matrix, is given by the expression:

$$Z_p(p) = R_e \frac{\coth U(p)}{U(p)} \quad (5.3)$$

$$U(p) = \sqrt{\frac{1}{\sigma''} \left(p\tau_1 + \frac{p\tau_2}{p\tau_3 + 1} \right)} \quad (5.4)$$

where $R_e = 1/\sigma'S$; $\sigma'' = 1/S$; $\tau_1 = R_e C_d$; $\tau_2 = R_e C_\phi$; $\tau_3 = R_t C_\phi$; $p = j\omega$; $j = \sqrt{-1}$. R_e refers to the electrolyte resistance inside the pores of the oxide film as well as the resistance of the porous matrix itself; C_d to the double layer capacitance; C_ϕ to the pseudocapacitance associated with Equation 5.2; R_t to the charge transfer resistance of Equation 5.2; S to the surface area of the porous electrode per unit length; and ω is the frequency of the a.c. signal. The equivalent circuit corresponding to the impedance expression given by Equation 5.3 is shown in Fig. 5.10.

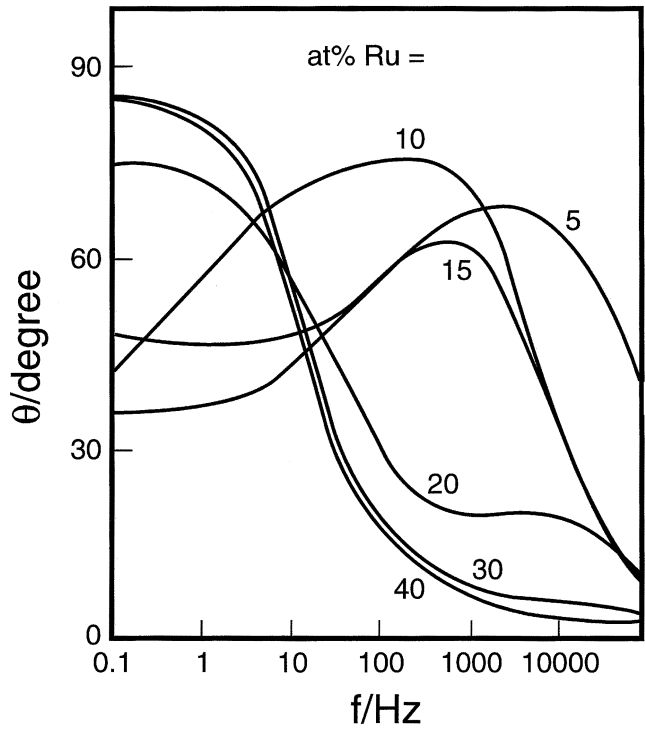


Fig. 5.9 Frequency dependence of impedance of fresh electrodes of different Ru content in 5 M NaCl at room temperature at OCP.

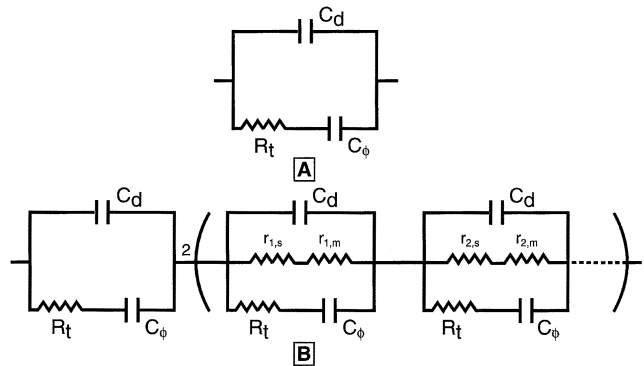


Fig. 5.10 Theoretical equivalent circuit for the reaction scheme $\text{Ru}_{\text{ad}}^{4+} + \text{e}^- \rightarrow \text{Ru}_{\text{ad}}^{3+}$ on (A) a planar electrode and (B) a porous electrode system.

The measured impedance, Z_r , generally includes the electrolyte resistance between the working electrode and the reference electrode, R_x , and hence

$$Z_T = R_x + Z_p \quad (5.5)$$

An analysis of Equation 5.3 shows that:

(1) When $\omega R_t C_\phi \ll 1$,

$$Z_T = R_x \quad (\text{resistive for } \omega \rightarrow \infty) \quad (5.6)$$

and

$$Z_T = R_x + R_e/p(C_d + C_\phi) \quad (\text{capacitive as } \omega \rightarrow 0) \quad (5.7)$$

This behaviour, depicted in Fig. 5.11 with the values calculated using Equation 5.3, represents the phase-angle variations exhibited by Ru/Ti electrodes containing 20–40 at.% Ru, which show low R_t values.

(2) When $R_e(C_d + C_\phi)^{-1} \ll (R_t C_d)^{-1} \ll (R_t C_\phi)^{-1}$, one will observe maxima and minima in the phase-angle plots. This is due to the progressive charging of the C_d and C_ϕ in the porous matrix, the time constants associated with these circuit elements being $R_t C_d$ and $R_t C_\phi$, respectively. Thus, as the R_t value increases or as the rate of the reaction given by Equation 5.2 decreases because of the lowered number of Ru sites in the Ru/Ti oxide film, the C_d is first charged resulting in a phase-angle of 90° . As the frequency is lowered or as time increases, the C_ϕ is finally charged resulting in the phase-angle of 90° . This behaviour is illustrated in Fig. 5.12.

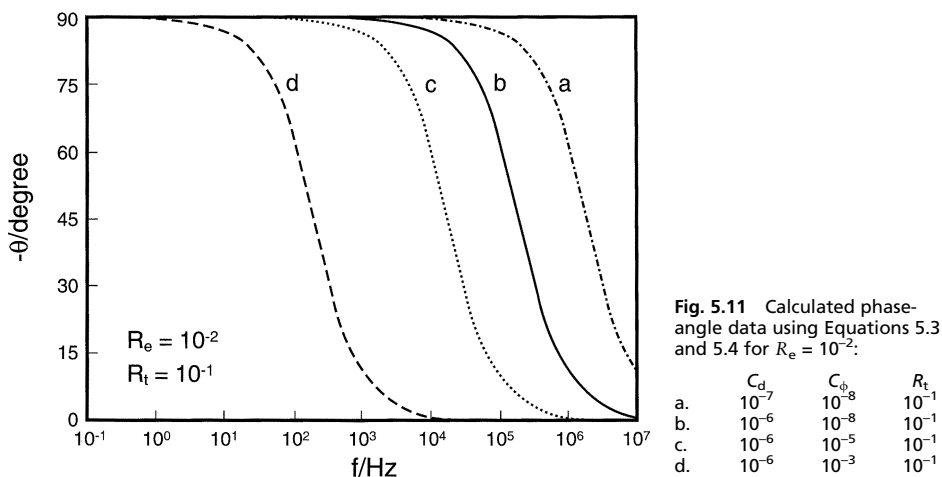


Fig. 5.11 Calculated phase-angle data using Equations 5.3 and 5.4 for $R_e = 10^{-2}$:

A complication that occurs on a low at.% Ru electrode is that, owing to the low Faradaic currents (low Ru content) and hence large R_t value, currents due to other trace redox reactions, e.g. oxygen reduction, become more detectable. This reveals itself in a phase-angle of 45° as $\omega \rightarrow 0$ as trace oxygen reduction would be diffusion-controlled. The impedance corresponding to this situation can be shown to be the same as that in Equation 5.3, with $U(p)$ expressed by the relationship:

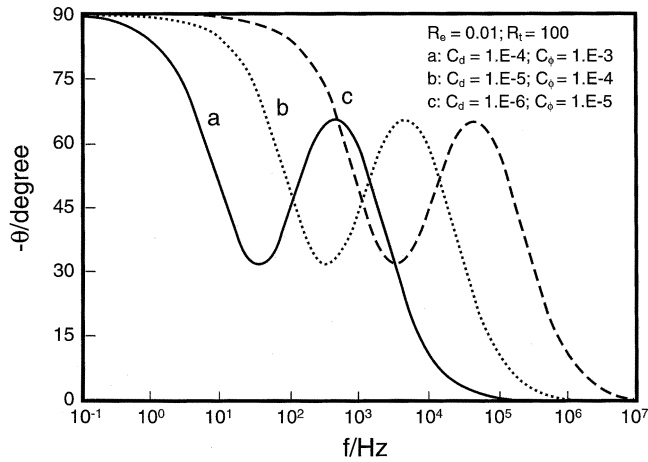


Fig. 5.12 Theoretical phase-angle plots using Equations 5.3 and 5.4 for $R_e = 10^{-2}$ and $R_t = 100$, along with the relevant ω values:

	C_d	C_ϕ	ω_a	ω_b	ω_c
a.	10^{-4}	10^{-3}	10^3	10	10^2
b.	10^{-5}	10^{-4}	10^6	10^2	10^3
c.	10^{-6}	10^{-5}	10^7	10^3	10^4

$$U(p) = \sqrt{\frac{1}{\sigma''} \left(p\tau_1 + \frac{p\tau'_2 + D\sqrt{p}}{1 + p\tau_3} \right)} \quad (5.8)$$

where $\tau'_2 = \tau_2(1 + a_1)$; $D = \tau_2 a_0$. The terms a_0 and a_1 arise from the relationship describing the Ru concentration changes with potential [44].

Figure 5.13 (curves a–c) depicts the calculated phase-angle data (using Equation 5.3), using circuit element values which might be typical of freshly formed 40, 30 and 20 at.% Ru coatings. R_e is very small, as these oxides are expected to be very conductive, so that the matrix resistance is very low. The C_d and C_ϕ values are both quite high, as the Ru content is high. The R_t value of 0.03 Ω and C_ϕ of 0.01 F (curve a, 40 at.% Ru), chosen for these calculations, is consistent with the values reported [4] for high at.% Ru electrodes. When the Ru content in the coating decreases, the pseudocapacitance decreases, and the charge transfer resistance associated with the Faradaic process of Equation 5.1 increases. This is consistent with the rationale of the lowered number of active Ru sites and hence lowered Faradaic currents under these conditions. Curves (d) and (e) in Fig. 5.13, calculated using Equations 5.3 and 5.8, demonstrate that the incorporation of a diffusion-like process in the case of freshly formed low at.% Ru coatings does indeed describe the experimental phase-angle behaviour (Fig. 5.9) well. The results in Fig. 5.13, thus, show that, as the at.% Ru decreases, for freshly formed films, C_ϕ decreases and R_t increases, and a maximum develops in the phase-angle plots. At low at.% Ru levels, diffusion of either H^+ in the Ru/Ti oxide solid state, or diffusion of trace

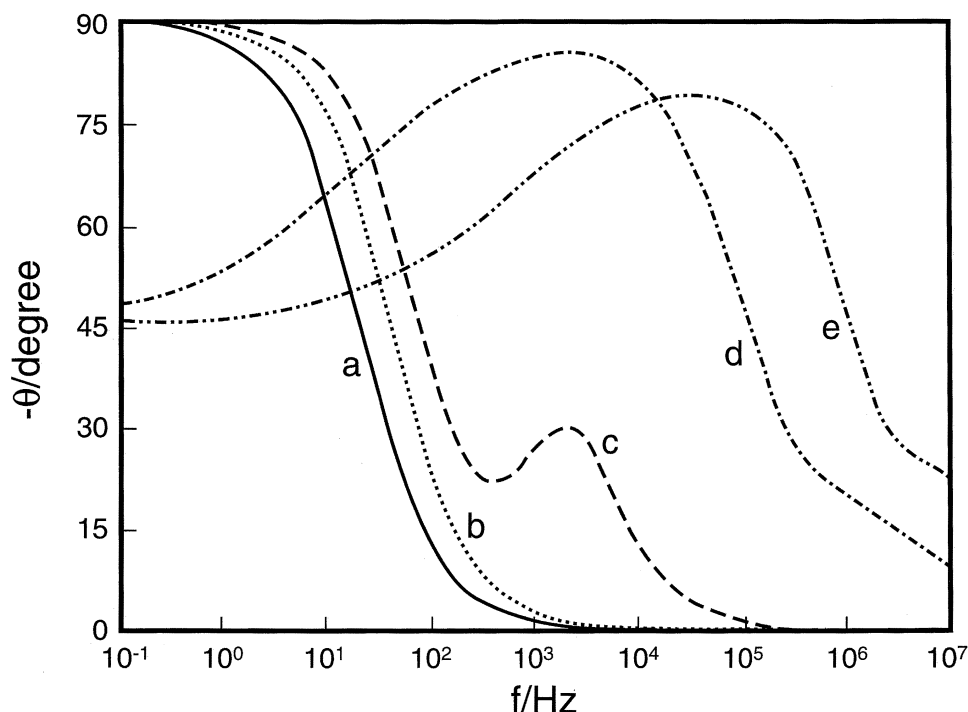


Fig. 5.13 Theoretical phase-angle plots using Equations 5.3 and 5.4 for a, b and c, and Equations 5.3 and 5.8 for d and e. Note that * indicates C_ϕ for these cases is equal to the value noted divided by $(a_1 + 1)$.

	R_e	C_d	$C_{\phi 2}$	R_t	D
a.	10^{-2}	10^{-4}	10^{-2}	3×10^{-2}	0
b.	10^{-2}	10^{-4}	5×10^{-3}	10^{-1}	0
c.	10^{-2}	10^{-4}	10^{-3}	10	0
d.*	15	10^{-6}	10^{-7}	2×10^2	6.5×10^{-5}
e.*	20	10^{-7}	10^{-8}	10^3	6.5×10^{-5}

species such as oxygen to the electrode surface, takes over, and the phase-angle then approaches 45° at low frequencies.

An analogous approach was made to attempt a better simulation of the impedance data for deactivated 30 at.% Ru films (Fig. 5.8). Figure 5.14 shows the phase-angle Bode plot, based on a range of circuit element values and including the low-frequency diffusional term, D . These results show that, with time of deactivation during chlorine evolution, the 30 at.% Ru electrode increasingly behaves like a low at.% Ru electrode (Fig. 5.9). The appearance of a maximum in the phase-angle plots at high frequencies as deactivation begins to occur is the result of a decreasing C_ϕ and an increasing R_t as a consequence of Ru depletion.

Thus, the polarisation data, cyclic voltammetric results and the a.c. impedance measurements all suggest that, when an $\text{RuO}_2/\text{TiO}_2$ anode exhibits a high over-potential, this is a direct consequence of the surface depletion of Ru. This is also consistent with the estimated R_e values of approximately $20\ \Omega$ for the failed electrodes, in contrast to the known, much higher specific resistivity of TiO_2 of

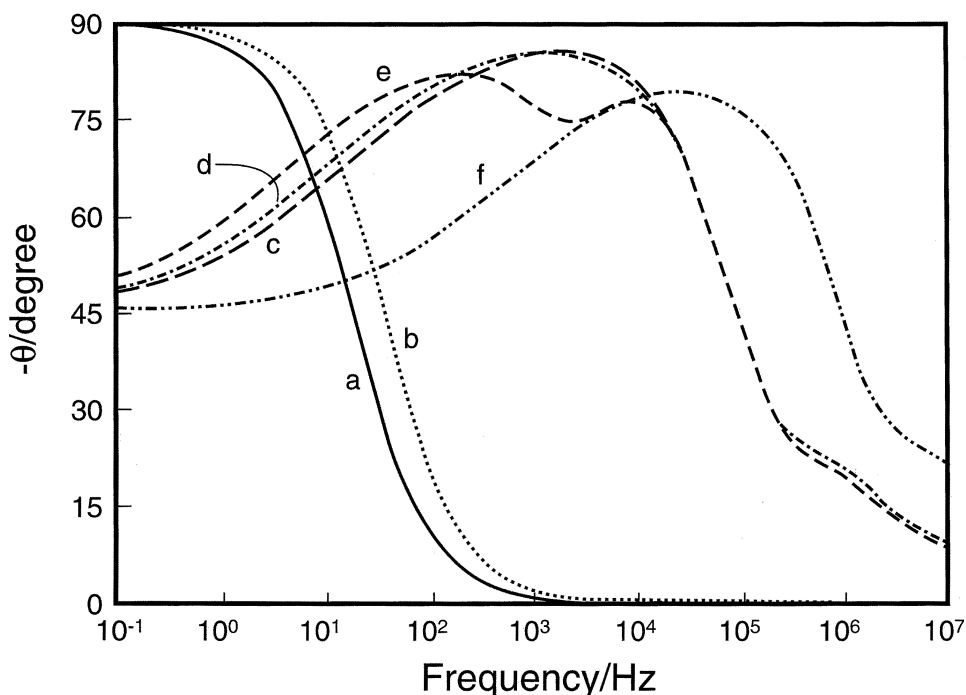


Fig. 5.14 Theoretical phase-angle plots simulating the experimental Bode plots during deactivation using Equations 5.3 and 5.8. Note that * indicates C_ϕ for these cases is equal to the value noted divided by $(a_1 + 1)$.

	R_e	C_d	C_ϕ	R_t	D
a.	10^{-2}	10^{-4}	10^{-2}	3×10^{-2}	0
b.	10^{-2}	10^{-4}	5×10^{-3}	10^{-1}	0
c.*	15	10^{-6}	10^{-7}	2×10^2	6.5×10^{-5}
d.*	18	10^{-6}	10^{-7}	5×10^2	6.5×10^{-5}
e.*	20	10^{-6}	5×10^{-8}	10^3	6.5×10^{-5}
f.*	20	10^{-7}	10^{-8}	10^3	6.5×10^{-5}

$10^{13} \Omega \cdot \text{cm}$. This suggests the absence of any build-up of a TiO_2 layer between the Ti substrate and the Ru/Ti oxide coating with the onset of anode deactivation. Furthermore, the similarity of the frequency response of a failed electrode to that of freshly prepared low at.% (c. 5–10 at.%) Ru electrodes at low frequencies, supports the conclusion of the absence of the build-up of a TiO_2 layer with failed electrodes.

5.3.2 Evidence for depletion of Ru from $\text{RuO}_2 + \text{TiO}_2$ coatings

The electrochemical characterisation studies, discussed in the previous section, showed that a 40 at.% Ru electrode, when subjected to extended electrolysis or potential or current cycling in NaCl solutions and when the chlorine overpotential reaches 300–400 mV, behaves like a fresh, low at.% Ru (about 5 at.%) electrode. This strongly suggests that Ru losses from the Ru/Ti oxide coating occur during electrolysis. To determine whether or not the Ru losses in failed anodes take place by uniform dissolution across the entire coating or whether only localised surface

depletion occurs, several anode samples were depth-profiled for Ru and Ti using secondary ion mass spectrometry (SIMS). Each sample was analysed at three different locations to ensure reproducibility. Comparison of the Ru concentration of fresh and deactivated anodes (both having Ru loadings of greater than 2 g m^{-2}) clearly shows that depletion of Ru occurs uniformly, but only through the outer $0.5\text{--}1 \mu\text{m}$ of the deactivated anodes (see Fig. 5.15). The SIMS data reported here are in agreement with those given previously [25]. It should be mentioned that the decreasing Ru concentration observed as the Ti substrate is approached, is an artefact arising from sputter-roughening and knock-on from the energetic primary ion beam.

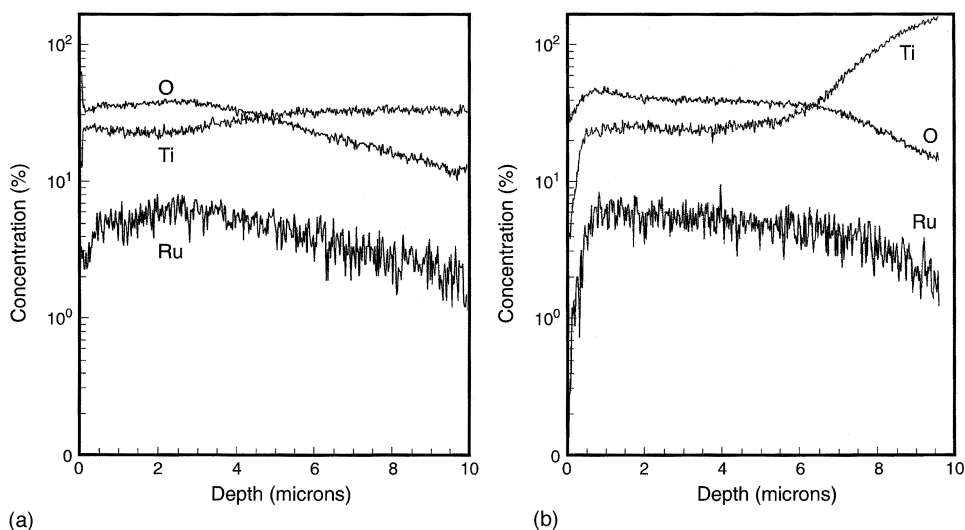


Fig. 5.15 SIMS profiles of (A) a new anode (Ru loading of 7 g m^{-2}) and (B) a failed anode (Ru loading of $3\text{--}4 \text{ g m}^{-2}$) from plant 1.

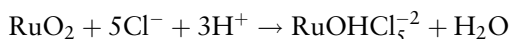
5.3.3 Origin of Ru losses

Ru losses can occur during electrolysis, as well as those due to shorting in mercury cell operations, from erosion, loss of Ru-based intermediates involved during the course of chlorine and oxygen evolution reactions and during shut-downs.

RuO_2 losses can occur by direct oxidation [9, 45] as:

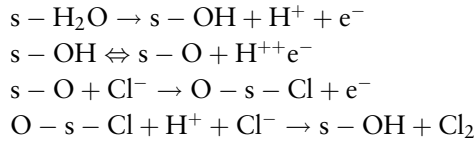


or via mechanisms involving the Cl^- ions to form soluble Ru complexes as:

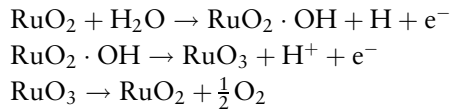


In addition, RuO_2 can also be removed from the coating during the chlorine evolution process via the oxidation of the adsorbed intermediates [2, 36, 46, 47] (i.e. s-OH ,

s-O, O-s-Cl), formed during the discharge of the chloride ions described by the following reaction scheme:



where s refers to a RuO₂ surface site. The depletion of Ru from the coating can also arise during the oxygen generation from the oxidation of the adsorbed intermediates (i.e. RuO₂·OH, RuO₃) formed during the course of the oxygen evolution, the mechanism of O₂ generation [36, 48, 49] being:



However, the published corrosion rates of Ru from oxygen evolution are not reliable, as they forecast [50] Ru losses as high as 40 g cm⁻² h, which is inconsistent with the anode lifetimes observed in commercial chlor-alkali cells.

Enhanced RuO₂ losses are also caused by shut-downs. Although the precise reason for this is not clear, this effect can result from the reverse currents arising from the dissolved chlorine, HOCl, and OCl⁻ present in the anolyte. The reverse current makes the anode cathodic, and reduces the RuO₂ to Ru or some lower oxidation state of the oxide (e.g. RuO_x where $x < 2$), which during electrolysis is oxidised to form a soluble Ru species such as H₂RuO₃, H₂RuO₅ or RuO₄²⁻. Alternatively, the surface oxidation state of RuO₂ may be modified during the current interruptions to an unstable intermediate, leading to its dissolution in the anolyte.

While it is unequivocally acknowledged that RuO₂ dissolves during the course of electrolysis in NaCl solutions, the individual reactions contributing to this are not known with certainty at present, owing to the difficulties in designing the relevant experiments. However, the progressive removal of the active layers, and the general dissolution due to the Ru losses from the chlorine evolution reaction can be calculated from data given elsewhere [24]. The dissolution rate of Ru (V_d in g cm⁻² h, due to the combined effect of erosion and general dissolution during electrolysis), was found to be high initially and decreases significantly with time (t in hours; see Fig. 5.16), following the relationship:

$$V_d = 2.5 \times 10^{-6} t^{-1.2} \quad (5.9)$$

Hence, the Ru losses, in g cm⁻², at time t , due to general corrosion can be given as:

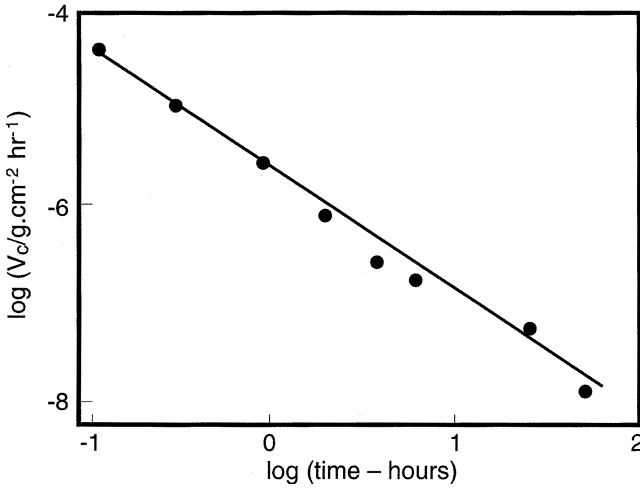


Fig. 5.16 Dissolution rate of 30% RuO₂ + 70% TiO₂ at 2 kA m⁻² in 300 g l⁻¹ NaCl at 70°C arising from erosion and general dissolution (plotted from the data in Ref. [24]).

$$q_d = \int_{0.1}^t V_d t = 1.25 \times 10^{-5} (1.5849 - t^{-0.2}) \quad (5.10)$$

The shut-down corrosion rate, V_s (in g cm⁻² h), obtained from previous data [22], can be expressed as:

$$V_s = (1.2 + 227n) \times 10^{-7} \quad (5.11)$$

where n refers to the number of shut-downs per month, each shut-down lasting for one hour. Hence, the Ru losses from the shut-downs will be:

$$q_s = V_s \times n = (1.67 + 0.315n) \times t \times n \times 10^{-10} \quad (5.12)$$

where the number of shut-downs at time t is $t \times n/720$. Hence, the total Ru loss over the time t is equal to $q_d + q_s$. From the total Ru loss, one can calculate the altered mol% RuO₂ in the loading and hence the anode potential, following the anode potential versus mol% RuO₂ (x) relationship developed from previous data [18]. One can now calculate the anode potential versus time, assuming the Ru loss occurs over the entire thickness of the coating or over 0.5 or 1 μm of the outer region of the anode coating:

$$E(V \text{ versus SCE}) = 1.3796 - 2.0538x + 5.8702x^2 - 8.3950x^3 + 5.8621x^4 - 1.5849x^5 \quad (5.13)$$

The results of the calculations reveal that the Ru losses from erosion, dissolution and open circuit corrosion (assuming shut-downs at a frequency of 12 per year), occurring

over the entire thickness of the coating, will not adversely affect the anode lifetime. However, if the Ru losses are occurring only over the thickness of a $0.5\text{--}1.0\text{ }\mu\text{m}$ layer on the top, as indicated by the SIMS data, then the lifetime projections show (Figs 5.17 and 5.18) escalated anode potential values over a relatively short period of time even though the overall Ru loading is still high ($>2\text{ g m}^{-2}$). Thus, it is the surface depletion of RuO_2 leading to the altered ratio of $\text{RuO}_2/\text{TiO}_2$ in these layers that results in the increased anode potentials. Note that the surface depletion of RuO_2 is exacerbated by shut-downs. Increased current interruptions during the first few years of active life is not significantly reflected in the anode potential variations as the mol% RuO_2 is still high in the surface region to allow the anode potential to vary. However, if the shut-down frequency increases when the surface mol% RuO_2 is low, as is the situation with an aged anode, it will result in a rapid escalation of the anode potential.

Thus, the SIMS studies and the approximate calculations presented above clearly

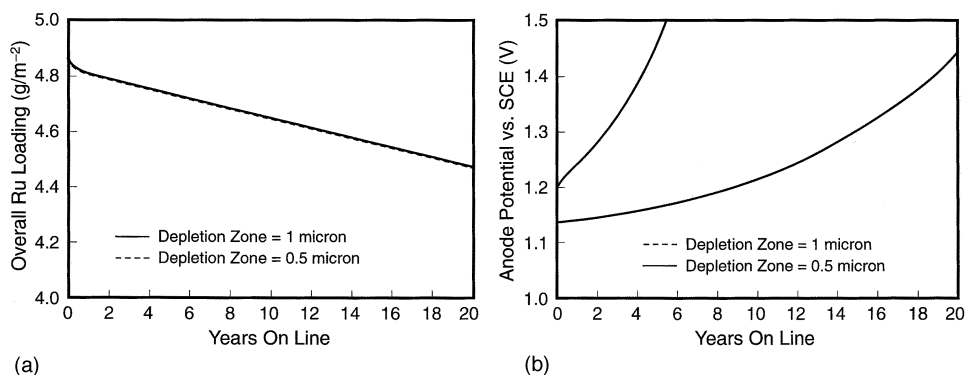


Fig. 5.17 Anode life calculations using Equations 5.10–5.13, assuming 12 shutdowns per year, for a coating composition of 30% RuO_2 + 70% TiO_2 (total Ru loading = 5 g m^{-2} ; coating thickness = $10\text{ }\mu\text{m}$; operating current density = 3 kA m^{-2}). (A) Overall loading versus time (in years); (B) anode potential versus time (in years).

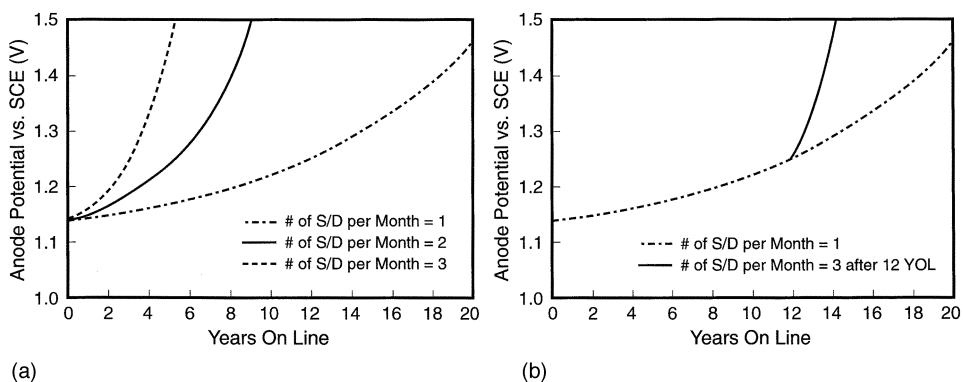


Fig. 5.18 Anode life calculations using Equations 5.10–5.13, with a depletion zone of $1\text{ }\mu\text{m}$, for a coating composition of 30% RuO_2 + 70% TiO_2 (total Ru loading = 5 g m^{-2} ; coating thickness = $10\text{ }\mu\text{m}$; operating current density = 3 kA m^{-2}). (A) Effect of shutdowns (S/D); (B) effect of increased shutdowns.

show the surface depletion of RuO_2 to be causal for the anodes to exhibit high anode potential, when the Ru loading is still high (i.e. $>2 \text{ g m}^{-2}$).

5.3.4 Strategies to prevent the loss of Ru content

As shown above, the lowered at.% RuO_2 in the outer region of the coating is the reason for the anode potential reaching unacceptable values, from a consideration of the operational economics. The decreasing Ru levels on the surface are a consequence of shut-downs, loss of Ru-based adsorbed intermediates involved in the chlorine and oxygen evolution reactions and erosion, in addition to the blockage of the active anode surface by the impurities in the solution. The latter can be minimised by using high-quality brine, devoid of impurities such as SiO_2 or SiO_3^{2-} , Mn^{2+} , Ba^{2+} , Fe^{2+} or Fe^{3+} using conventional techniques [51, 52] such as addition of MgCl_2 to remove silica-based species and operating the ion-exchange columns to remove the cations at the proper pH values. The Ru losses arising from erosion by the chlorine gas generated at the anode can be lowered by operating the cells at low current density. However, this may not be a practical option, as the present trend is to operate the cells at as high a current density as the system permits. The loss of Ru during shut-downs can be substantially reduced by minimising the shut-downs or by negating the effect of shut-downs by cathodic protection or by a rapid hypo kill operation. This would preserve the surface compositional integrity of the anode coating. In addition, operating the cells in the pH region of 2–3 will also be beneficial in terms of lowering the Ru losses from the coatings for two plausible reasons. Firstly, electrolysis in the low pH range of 2–3 will also dissolve TiO_2 , which will result in minimal changes in the surface composition of the coating. Secondly, in the low pH region, the percentage O_2 evolving at the anode will be lower because of thermodynamic and kinetic considerations [51] and hence Ru losses via the oxygen evolution reaction can be decreased.

Another option to lower the Ru losses is to dope the anode coatings with IrO_2 , which has been shown [53, 54] to markedly decrease the Ru corrosion rate during electrolysis in NaCl solutions. This would minimise the surface depletion of Ru, as shown by the SIMS analysis of the $\text{TiO}_2 + \text{RuO}_2 + \text{IrO}_2$ coatings (Fig. 5.19), and thus extend the operating life of the anodes.

5.3.5 Rejuvenation of deactivated RuO_2 anodes

If the Ru loss in the deactivated anode is a result of uniform dissolution across the entire coating layer, resulting in a Ru loading of less than 2 g m^{-2} , the anode has to be recoated to regain its electrocatalytic activity for the chlorine evolution reaction. Under these conditions, the existing anode coating must be stripped prior to recoating. However, if surface depletion of Ru is the cause for increased anode potential, then replenishment of these surface sites should result in the rejuvenation of the deactivated anodes.

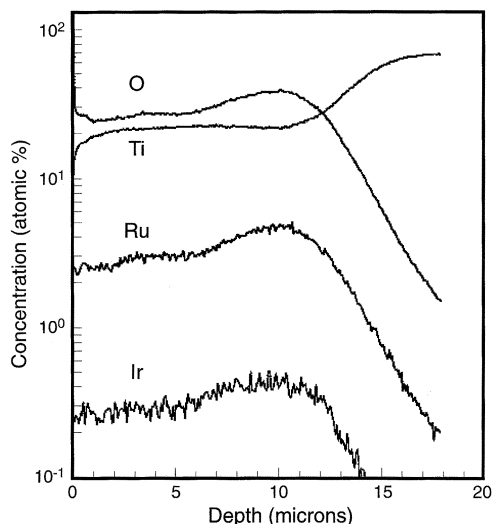


Fig. 5.19 SIMS profile of $\text{IrO}_2 + \text{RuO}_2 + \text{TiO}_2$ after 1000 days of operation at plant 2.

Recent studies performed with deactivated anodes show [55] that electroless or electrolytic platinum deposition on failed anodes, not only lowered the polarisation behaviour of these anodes (see Fig. 5.20), but also demonstrated an equivalent life-time as that of a new anode in accelerated life tests in the sulphuric acid solution (see Fig. 5.21). These results unequivocally demonstrate that the deactivation of anodes, for which the Ru loading is still high, is a direct consequence of the depletion of Ru from the outer region of the anode coating. Note that this process of surface enrichment by conducting electroactive species will not lead to reactivating a failed anode, if there is a TiO_2 build-up at the Ti substrate/coating interface.

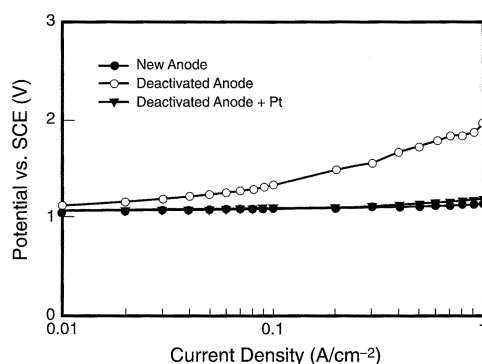


Fig. 5.20 Effect of Pt-doping on the anode potential using samples from plant 3.

Scanning tunnelling microscopic studies [56] show (Fig. 5.22) that the extent of the surface which is conducting is approximately 13%, whereas the same anode, after deactivation in sulphuric acid solution, exhibited a conducting region of only 6%. However, after Pt-doping of the failed anode, the conducting fraction of the surface increased to 17%. This suggests that Pt deposition serves to replenish the deactivated

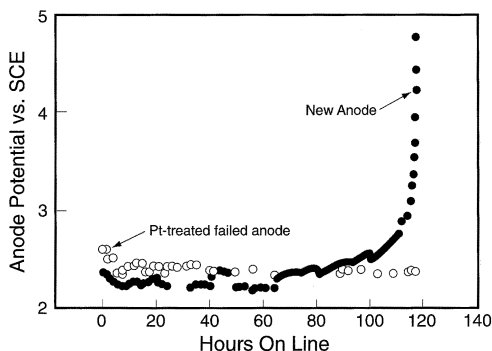


Fig. 5.21 Accelerated life tests in 0.5 M sulphuric acid at 5 kA m^{-2}

surface regions, by enhancing the surface conductivity as well as electrocatalytic activity of these electrodes. Recent plant tests conducted with Pt-coated ‘failed anodes’ in diaphragm cells showed their performance to be equivalent to that of a new anode, over 2.5 years of operation.

5.4 Summary and conclusions

Electrochemical characterisation studies employing anodic polarisation data, cyclic voltammetry and a.c. impedance with fresh Ru/Ti oxide electrodes containing varying atomic percentages of Ru, and with a 40 at.% Ru electrode, deactivated using potential and current cycling, revealed that a failed electrode behaves like a fresh low at.% Ru electrode. The decrease in the at.% Ru from a 40 at.% Ru electrode was traced to the Ru losses occurring during the course of the chlorine evolution and oxygen evolution reactions (via the loss of the unstable Ru-based intermediates involved in these reactions) and during shut-downs. The Ru depletion was found to be confined to the top $0.5 \mu\text{m}$ of the coating by SIMS studies, complemented by lifetime calculations. It was shown that the Ru depletion leading to the decreased at.% Ru in the surface region will result in the decreased conductivity of the surface layers, culminating in a change in the mechanism of the chlorine evolution reaction and hence the increase in the anode potential. Replenishment of the failed anode surface by providing surface conductivity and electrocatalytic activity by Pt-doping of the surface layers was shown to provide anode lifetimes and anode overpotentials similar to that of a new, high at.% Ru anode.

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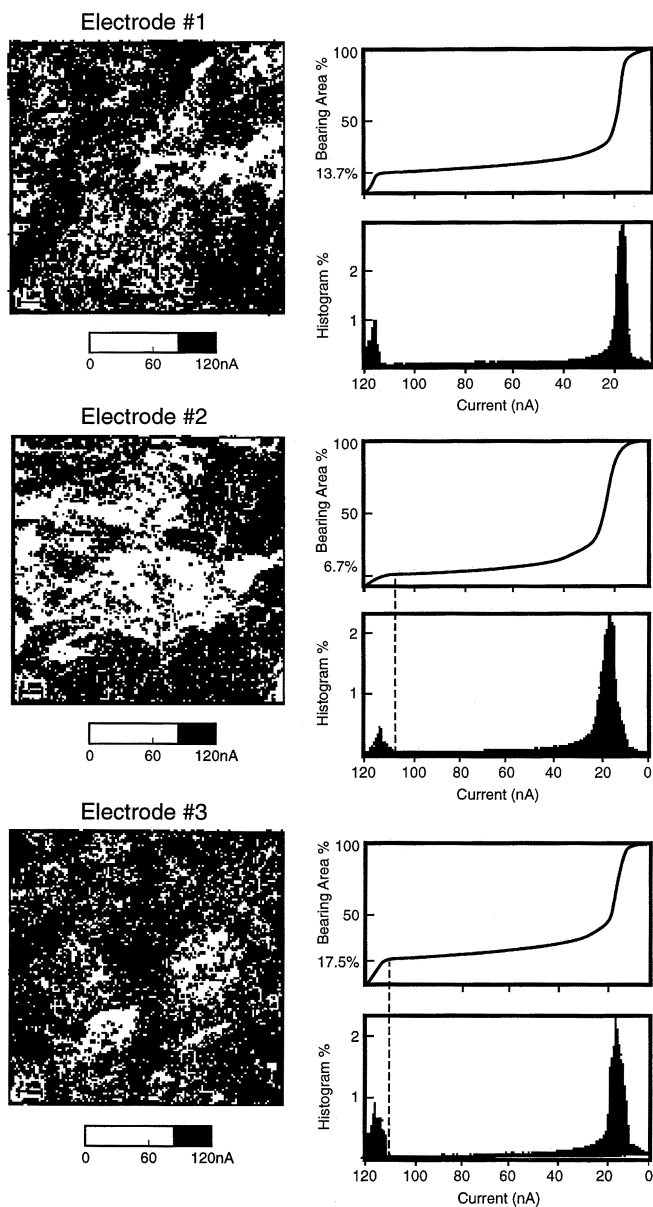


Fig. 5.22 STM current distribution of electrodes (in the left column). Electrode 1: new anode; Electrode 2: new anode deactivated in H_2SO_4 ; Electrode 3: Pt-coated failed anode. The black dots correspond to tunnelling current larger than 90 nA. In the right column are the corresponding histograms and conductive percentage area calculations. Source: Ref. [56], reproduced with permission from the author and the publisher, Springer-Verlag.

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Chapter 6

High Current Density Operation of Chlor-Alkali Electrolysers – the Standard for the New Millennium

W C Meadowcroft and R D Theobald

6.1 Introduction

High current density has become a reality in the chlor-alkali industry. More than half of the plants starting up between 1997 and the end of 2000 are designed for operation at 4–6 kA m⁻². Furthermore, many plants designed for operation up to 4 kA m⁻² are successfully operating at higher current densities to meet increased demands, or to displace expansion projects.

DuPont research into high current density and the associated effect on membrane and electrolyser performance has been underway for a decade. It has been the area of greatest concentration for the company during the last 5 years. Studies at the DuPont Experimental Station and Fayetteville Nafion® Customer Service Laboratories resulted in polymer innovation and new membrane designs. This work has also identified interactions between membranes and electrolyzers

This chapter discusses the work at DuPont and provides a simple set of tools to explore the interactions between membranes and electrolyzers at high current densities. In fact, these tools help to provide the answer to the following question:

How is cell voltage and total electrolyser performance affected by these interactions and how can it be used to monitor and improve operations?

DuPont's perspective on membrane development will be outlined. The expansion of the facilities at the Nafion® Customer Service Laboratory will also be described. This expansion has been undertaken in support of DuPont's commitment to increase the understanding of chlor-alkali technology and ensure continuous improvement of DuPont's membranes.

6.2 The boundary layers

Production of caustic and chlorine by the membrane process is typically depicted as a simplistic process (see Fig. 6.1). Chloride is oxidised and water is reduced; caustic,

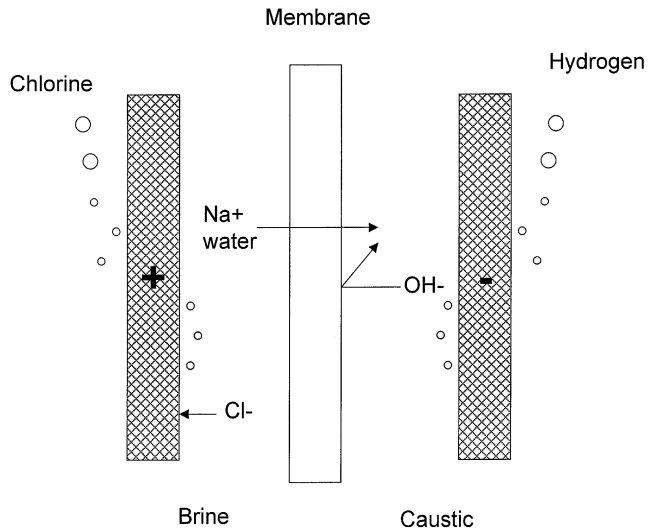


Fig. 6.1 Scheme of the membrane procedure for producing caustic and chlorine.

chlorine and hydrogen are produced. The interactions between membranes and electrodes are not recognised; however, it is known that boundary layers exist on membrane surfaces and on each working electrode.

The oxidation of chloride at the anode results in an anode boundary layer that contains less chloride than the bulk anolyte (Fig. 6.2). The membrane is pressed against the anode by differential pressure, and thus is integrated into the anode boundary layer. Good internal mixing is necessary to minimise the layer effect and to maintain a steady supply of chloride to the anode for reaction. The ionic concentration and the thickness of this layer will have an effect on the water content, the

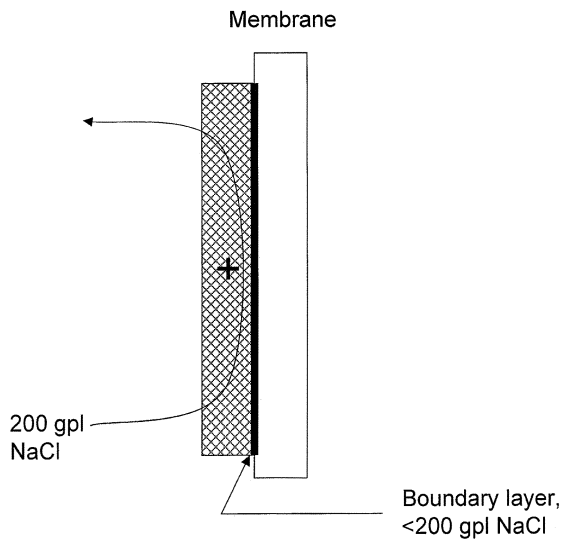


Fig. 6.2 Representation of the membrane anode boundary layer.

water transport and, ultimately, the electrical resistance and efficiency of the membrane. Preliminary data indicate that a relationship exists between anode gap, water transport and current efficiency. More work is underway to improve understanding and quantification of this effect.

On the cathodic side, the interactions are more complex (Fig. 6.3). Most membrane cells producing 32 wt.% caustic soda at 85–90°C and with a bulk anolyte concentration of 200 g l⁻¹ NaCl will have a water transport value of 3.8–4.0 mol of water per mol of sodium ion transported. When the ratio is calculated, the result shows that the caustic formed at the cathode surface of the membrane has a strength of 36–37 wt.%. This strong caustic forms a boundary layer on the cathode surface of the membrane. The thickness of this boundary layer is dependent on the efficiency at which the bulk catholyte can sweep the cathode surface and stir the strong caustic into the bulk. If this layer becomes too thick or too strong, the water content of the polymer at the cathode surface of the membrane will be reduced. This can lead to higher membrane resistance and the potential for membrane damage owing to ohmic overheating of the carboxylic layer. The layer itself will have a contribution to the total cell voltage due to its higher resistance.

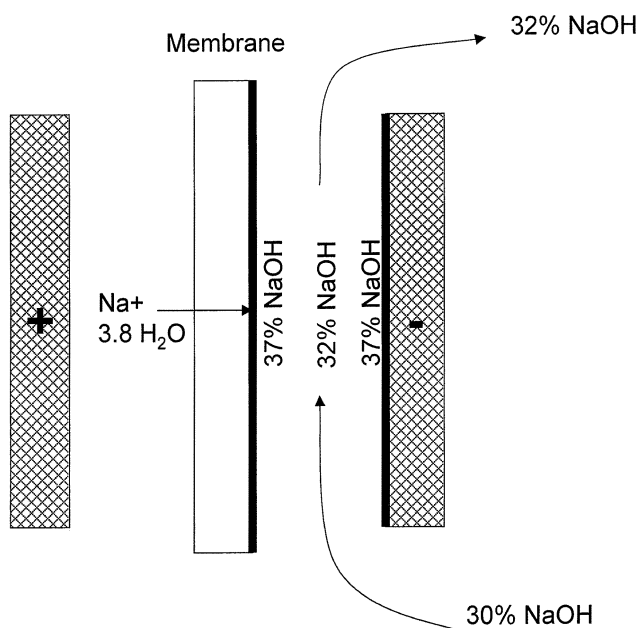


Fig. 6.3 The more complex chemical interactions at the membrane cathode.

The working cathode also generates a boundary layer. The water that is reduced at the cathode is supplied by the bulk catholyte. This stripping effect forms a layer of approximately 37 wt.% caustic on the surface of the cathode. Again, the thickness of this layer is determined by the efficiency of the internal mixing within the cathode compartment.

Modern high performance electrolyzers are designed to operate at high current densities and zero or very narrow gap to reduce the IR drop across the catholyte. This arrangement brings the boundary layers of the membrane and cathode into close proximity. In some cases, the layers contact each other. These electrolyzers require high rates of internal mixing with a very high rate of bulk impingement on the membrane and cathode to reduce the thickness of the layers to the absolute minimum. If mixing is insufficient, the layers will meld and form a pool of strong, viscous caustic between the membrane and the cathode. The cathode reaction may draw water from the combined layers resulting in an even stronger layer (Fig. 6.4). This condition will result in performance issues.

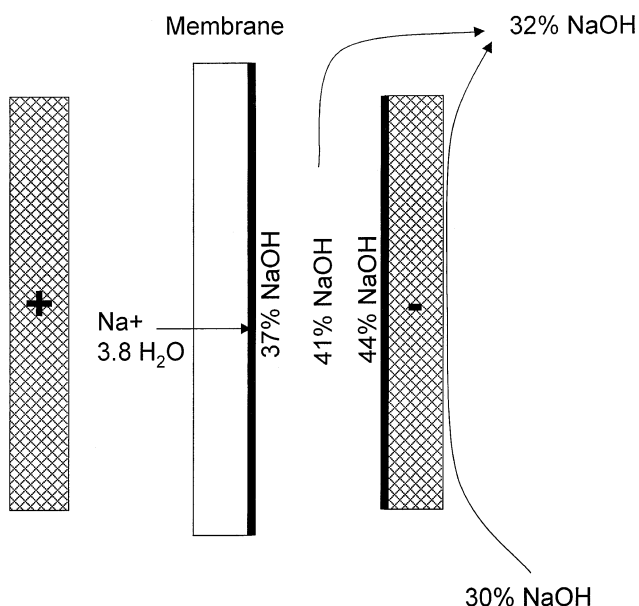


Fig. 6.4 Scheme illustrating how the chemical interactions result in cathode performance issues.

6.3 Tools for operations and research

By understanding the boundary layers and the general operating condition limits, plant operators can optimise performance. Small incremental adjustments to the dependent variables, current density and electrolyte concentrations will provide linear plots of the independent variables, voltage and current efficiency, in the safe operating zone. Non-linearity will occur when a limit is reached.

6.3.1 Current density versus voltage

Baseline data must be generated within the normal current densities at which the plant operates. Voltage data should be collected at various current densities and plotted. A

linear regression analysis will yield the slope and intercept data. The slope, or k-factor, is the membrane contribution. High performance membranes for high current density operation should have a slope of 120–160 mV kA⁻¹. The intercept is the electrolyser contribution and should be in the range of 2.43–2.48 V.

6.3.2 Caustic concentration versus voltage and current efficiency

A procedure has been devised to test the membrane and cathode boundary layer interactions to determine if there is a limit within the normal caustic operating range. Making small, incremental adjustments to the product caustic strength carries out this testing. This testing should start at a value lower than the current operating level of 29–30 wt.%. All other dependent variables should be maintained at normal values. When equilibrated, concentration, voltage and current efficiency data are recorded. The product caustic strength should then be increased by approximately 1% and the test procedure repeated until the product caustic reaches a value of 32.5–33 wt.%. The data are then plotted and tested for linearity. The typical response of voltage versus caustic concentration is an increase of 15–20 mV for every increase in wt.% of caustic. Higher values and/or non-linearity will indicate that a limit has been reached. Current efficiency should remain fairly flat in the 29–33 wt.% range.

6.3.3 Brine concentration versus voltage and current efficiency

Making incremental adjustments to the exit brine strength will test the effect of the anode/membrane boundary layer. By starting at a value lower than the current operating level of approximately 190 g l⁻¹, all other dependent variables should be maintained at their normal values. When equilibrated, concentration, voltage and current efficiency data are recorded. The exit brine strength should then be increased by approximately 10 g l⁻¹ and the procedure repeated until the exit brine strength reaches 210–220 g l⁻¹. By plotting the data linearity can be tested. The typical response of voltage versus exit brine strength is an increase of 1 mV for every 1 g l⁻¹ increase in brine strength. Higher or lower values and/or non-linearity will indicate that a limit has been reached. The current efficiency should be fairly flat in the range of 190–210 g l⁻¹. A slight increase in efficiency may be noted at 220 g l⁻¹.

6.3.4 Conclusion

If all responses to these tests are linear and typical, and all other independent variables remain within normal operating specifications, it can be assumed that the membrane and electrolyser interactions are optimised for operation within the current density range tested in Section 6.3.1. This procedure has been used successfully to diagnose and optimise operating conditions for both standard and high current density operations where unexpected performance issues have arisen. Furthermore, operators

who wish to explore higher current density operation can use these tools to examine performance and membrane/electrode interactions as current density is incrementally increased.

6.4 Boundary layer and membrane design

6.4.1 Membrane construction and design

High performance Nafion® membranes for high current density applications have been designed to promote and enhance mixing of the bulk electrolytes into the boundary layers of the anode and cathode surfaces of the membranes. Smooth, flat cathode surfaces yield a cathode-side boundary layer of uniform thickness that is more efficiently and effectively stirred. The uniformity of the layer also contributes to uniform current distribution across the membrane. DuPont's unique anode surface geometry promotes circulation of anolyte between the membrane and the anode. This helps to ensure that all areas of the working anode are constantly and uniformly refreshed so that water transport and current distribution remain homogeneous across the membrane. The highly developed reinforcement fibre used in the design is located near the anode surface to provide homogeneous current distribution across the high-resistance carboxylic layer, thus utilising its full potential and providing very low k-factors that are essential for high current density operation. Advances in low-voltage polymers that maintain high current efficiency are being made continually and the advantages of these are now being enjoyed and expected by the chlor-alkali industry.

6.4.2 Membrane design results

As a result of flat design, enhanced fibres, and low-voltage polymer, DuPont now offers products that include:

- N981 ($V = 2.95$ at 3.1 kA m^{-2} and a k-factor of 0.130)
- N982 ($V = 2.95$ at 3.1 kA m^{-2} and a k-factor of 0.130)
- N2010 ($V = 2.89$ at 3.1 kA m^{-2} and a k-factor of 0.120)

6.5 A new laboratory for the millennium

In its support of the commitment to increase the understanding of chlor-alkali technology and to continuously improve its membranes, DuPont has expanded its CSL (Customer Service Laboratory) facilities at Fayetteville, North Carolina in the United States.

Prior to 1999, DuPont maintained laboratories at both ESL (Experimental Station Laboratories) in Wilmington, Delaware and the CSL (Customer Service Laboratory) in Fayetteville. In preparing for the new millennium, DuPont's business plan has provided for moving the main research function to Fayetteville and consolidating the laboratories there. These facilities are also now showing their age after a combined 35 years of round-the-clock operation.

6.5.1 Laboratory planning phase

In its planning phase DuPont has prepared to:

- expand the test-cell facilities at CSL to include 64 three-inch test cells
- rebuild the cell tables with corrosion-resistant FRP material
- replace and upgrade the ageing distributed control system
- increase the number of research hoods available in the wet laboratory
- devise a scheme to limit shut-down time to two weeks since many facets of manufacturing, research, and technical service rely on the laboratory facilities
- move the 0.21 m² pilot cell to Fayetteville
- provide separate rooms adjacent to the cell room for control and electrical/instrument components.

6.5.2 Laboratory construction

The most challenging objective has been to limit downtime. To accomplish this ideal, DuPont has:

- prefabricated new cell tables from FRP frames and pre-wired them at the Fluor Daniel construction facility;
- simultaneously installed a new Bailey distributed control system and wired this to junction boxes in the ceiling above the operating cell room. Operation of the wiring between the new distributed control system and the new junction boxes was checked before proceeding.

In June 1998, DuPont was shut down and during the planned two week outage the company accomplished its objectives of installing the new equipment and connecting it to the distributed control system, which had been previously installed and partially checked prior to the outage.

The final phase was completed in May 1999, with the installation of a full-size, commercial pilot cell to enhance the membrane testing capabilities. It is now possible to achieve steady state with the computer-controlled 0.21 m² electrolyser in just a few hours and operators can obtain meaningful performance test data in 2–3 days.

6.5.3 Current laboratory status

DuPont's laboratory assets now include:

- membrane inspection table
- membrane leak tester
- 64 three-inch test cells to determine voltage and current efficiency at current densities from 3.1 kA m^{-2} to over 7 kA m^{-2}
- facilities to feed KCl to a variable number of the 64 test cells
- facilities to feed spiked brine to a variable number of the 64 test cells
- 24 ft of research hood for R&D
- ICP for brine analysis and membrane extractions
- a colorimeter for brine purity testing
- an SEM (scanning electron microscope) with XRF (X-ray fluorescence) capability
- a 0.21 m^2 pilot cell for further testing of new membrane developments
- a modern control system.

This laboratory serves the chlor-alkali industry in many ways. These services include:

- operations to determine chlor-alkali performance parameters of current production
- research to determine the performance of new membranes
- a technical service to determine the effects of impurities and operating conditions on membranes
- the routine analysis of customer returns or answering performance questions.

The nice thing about the DuPont Laboratory in Fayetteville is that the reader is invited to visit us there.

Chapter 7

Chlorine Processing Beyond the Millennium – the Use of Gas-separation Membranes

T F O'Brien

7.1 Introduction

Electric energy is the predominant cost in the manufacture of chlorine and is the driver for most of the technical progress in the chlor-alkali industry. The busiest areas of development over the past 20 or 30 years have been related to reductions in energy consumption. Approximately 60% of the papers presented in this book deal with improvements in chlor-alkali cell internals, namely the anolyte/catholyte separator (primarily membranes) and the electrodes.

The stringent requirements for brine purity imposed by membrane cells have also led to some cost-reduction efforts in that area. Chlorine processing, on the other hand, has been somewhat neglected. A technologist absent from the chlor-alkali industry since 1970 would be impressed with changes in the cells and in brine treatment but would find few surprises in a review of the design of the gas-processing sections of today's newest plants. The most significant changes would be in materials of construction and in simplifications made possible by improvements in the electrolytic plant, notably by adoption of permanent metal anodes.

Whilst improvements have been made in the efficiency of some individual items, the components of the standard block flow-diagram of Fig. 7.1 have changed little over the years. In this chapter, the potential improvements offered by a new concept in operation are considered. The subject here is a different kind of membrane that allows the gas-phase separation of chlorine from some of its accompanying impurities.

First, the aspects of the chlorine process that make it a candidate for membrane

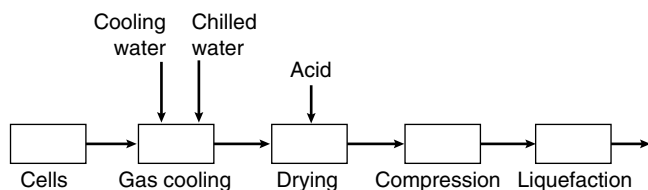


Fig. 7.1 Chlorine gas processing.

processing will be looked at. After a very brief review of the fundamentals of membrane separations, test results and possible applications are discussed. The applications include the enhancement of liquefaction systems and the upgrading of compressed chlorine gas to make it suitable for production of ethylene dichloride. Finally, rough economic comparisons of membrane processing with alternative methods of handling liquefaction tail gas are presented.

7.2 Aspects of chlorine processing

7.2.1 The components of chlorine process gas

Since chlorine is produced from aqueous solution, the gas issuing from the cells is saturated with water. Oxygen is produced in the cells through electrochemical inefficiencies. In membrane cells, for example, there will be a certain amount of leakage of hydroxide ions produced at the cathodes back through the membranes. At the anodes, these ions can produce oxygen gas by direct electrochemical oxidation. Hydrogen will also be present in the chlorine, either through leakage from the cathode side of the cells or by electrochemical production at cathodic spots on the anode side. Less hydrogen is produced in membrane cells than in the older types.

The feed brine is also a source of impurities. It can contain dissolved and entrained air and so can contribute oxygen and nitrogen. The brine may also contain carbonate that was added during chemical treatment in order to remove dissolved calcium. The carbonate will be converted to carbon dioxide in the cell environment.

Finally, there are many opportunities in the typical process for air or nitrogen to enter the gas stream. These have been described elsewhere [1], and here we mention by way of example the gas (nitrogen or dry air) used to pad the labyrinth seals on the typical centrifugal chlorine compressor.

The contaminants oxygen, nitrogen, hydrogen, and carbon dioxide are considered in this chapter.

7.2.2 Physical separations in chlorine processing

Separations of materials occur at several points in the typical chlorine gas processing system. Usually, cell gas first is cooled, removing much of the water evaporated from the cells. As suggested in Fig. 7.1, this may be completed in two stages, using chilled water in the second to enhance the condensation of water [2]. Cooling is followed by contact with concentrated sulphuric acid, giving a gas with less than 50 ppm of water and so considered 'dry'.

The dry chlorine may be compressed and cooled in order to liquefy it. Liquefaction is essential to the merchant production of chlorine. It is also sometimes practised in order to enhance the purity of the chlorine sent to further processing. Liquefaction,

too, is a separation process, removing chlorine selectively from the non-condensable gases that invariably accompany it. The gas leaving the liquefaction system is the topic of the next subsection.

The configuration of liquefaction systems is quite variable. Figure 7.2 shows a basic two-stage compression/liquefaction system. The pressure is higher in the second stage than in the first. Alternatively, the interstage compressor might be removed and a second, colder refrigerant used on the second liquefier. A third stage of liquefaction may also be used, operating at lower temperature and higher pressure than the first.

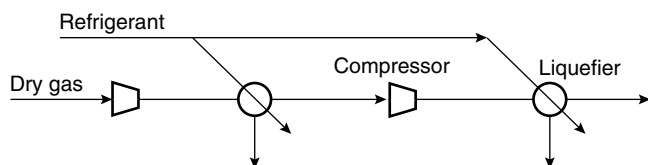


Fig. 7.2 Basic two-stage liquefaction process.

Liquefaction systems can be quite complex and expensive. Economic balances and local considerations determine the numbers of stages used and the combinations of temperature and pressure. The temperatures employed usually range from zero to -60°C or lower. The running cost of the energy supply can become quite high. The high capital and operating costs provide an opportunity for the application of membranes.

7.2.3 Disposal of uncondensed chlorine

Liquefaction of chlorine is always incomplete, because the non-condensable impurities carry chlorine at its vapour pressure as they leave the liquefaction process. This exit gas, or tail gas, is handled in any of several different ways. It is of course an intolerable plant emission, and the contained chlorine must at least be destroyed before the gas is released to the atmosphere. There is also a powerful economic incentive for recovering much of the chlorine in some usable form – Silver’s estimate of the value of the chlorine in the tail gas produced in the United States alone in 1981 was \$50 million [3].

The chlorine value can be converted into hypochlorite bleach by absorption into lime or caustic soda. It can also be used to produce hydrogen chloride by combining with hydrogen in a burner. The latter technique is particularly useful when the acid can be consumed on site in brine acidification or ion-exchange resin regeneration. Another approach that has found some favour in the past is the absorption of the chlorine into a solvent from which it could then be stripped and returned to the liquefaction plant.

In a 1991 survey of the plants of one licensor, Liederbach [4] reported that none of the three options named above predominated; they were chosen in roughly equal numbers. For various technical, environmental and marketing reasons, these disposal routes are not reliably available to all producers. In the absorption process, for

example, carbon tetrachloride has the best physical properties for the application and so was the solvent of choice. However, the use of carbon tetrachloride is no longer acceptable, and several of these systems have already been retired.

The great advantage of the absorption process over the synthesis of a by-product was its direct recovery of chlorine. Such a process or one that uses chlorine in another on-site process with steady demand is the ideal. More vigorous liquefaction is one approach to reducing the amount of chlorine value to be disposed of, and it has usually been chosen as the substitute for absorption. In this chapter, we discuss the use of gas-separation membranes as an alternative.

At the end of the chapter, we compare the use of membranes with the HCl and bleach processes and with an enhanced liquefaction process in which a third stage is added to an operating two-stage system.

7.3 Membrane considerations

7.3.1 Membranes in gas separations

Membrane gas-separation systems have found their first applications in the recovery of organics from process vents and effluent air [5]. More than a hundred systems have been installed in the past few years. The technique itself therefore has a solid commercial background. Membranes are assembled typically in spiral-wound modules, as shown in Fig. 7.3. Sheets of membrane interlayered with spacers are wound around a perforated central pipe. The gas mixture to be processed is fed into the annulus between the module housing and the pipe, which becomes a collector for the permeate. The spacers serve to create channels for the gas flow. The membranes separate the feed side from the permeate side.

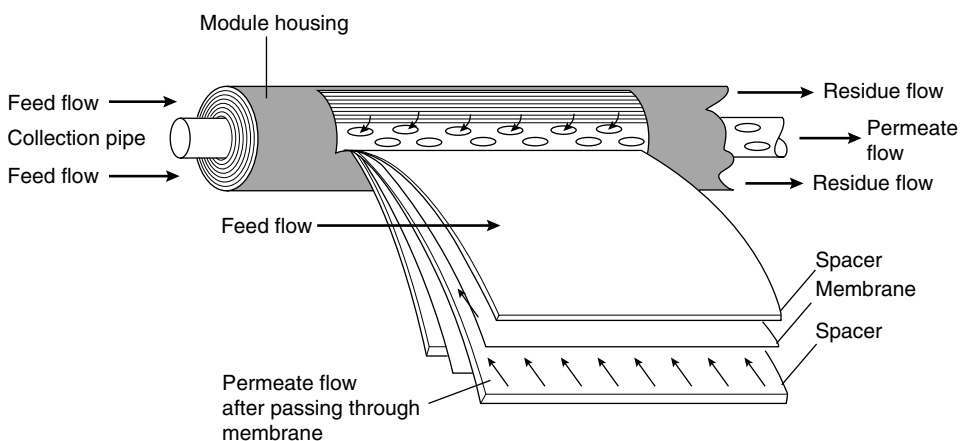


Fig 7.3 Membrane module construction. Courtesy of the American Chemical Society.

The mechanism for passage through the membrane involves dissolution in the polymer followed by diffusion under the influence of a concentration gradient. Permeability itself is the product of diffusivity and solubility:

$$P = D \times S$$

where P is the permeability (cm^3 gas per cm-s-cm Hg), D is the diffusivity of gas in the membrane ($\text{cm}^2 \text{ s}^{-1}$), and S is the solubility of gas in the membrane (cm^3 gas per $\text{cm}^3\text{-cm Hg}$).

A form of Fick's law gives the transport of a single component through a membrane:

$$J = DS\Delta p/t$$

where J is the membrane flux (cm^3 gas per $\text{cm}^2\text{-s}$), Δp is the partial pressure difference across the membrane (cm Hg), and t is the membrane thickness (cm).

The selectivity of a membrane for one of a pair of gases is expressed as the ratio of its permeabilities for the gases:

$$\alpha = P_1/P_2$$

Permeabilities measured for pure gases can serve as a rough guide for selection of membrane materials. For design, data must be obtained on gas mixtures, where selectivities are often found to be much lower than those calculated from pure-component measurements. This effect is often due to plasticisation of the membrane by sorption of the most soluble component of the gas. This allows easier penetration by the less-permeable components. The problem of concentration polarisation, which is often encountered in small-scale flow tests, may also be responsible. Concentration polarisation results when the retention time of the gas in contact with the membrane is long. This allows substantial depletion of the most permeable component on the feed side of the membrane. The membrane-surface concentration of that component, and therefore its flux through the membrane, decreases.

7.3.2 Membranes in chlorine processing

From the definitions of selectivity and permeability given in Section 7.3.1, it is possible to write:

$$\alpha = (D_1/D_2) \times (S_1/S_2)$$

Diffusion coefficients are of course greater for the relatively small molecules of the contaminants than they are for chlorine. Taking chlorine as component 1, it follows that in every case $D_1/D_2 < 1$. Unfortunately, this ratio is opposite to that we find for

solubility in commercially useful membranes: $S_1/S_2 > 1$. Successful operation therefore depends on a sufficiently high solubility of chlorine to offset the diffusional advantages of the other components.

Lokhandwala *et al.* [6] have reported field and laboratory work on the recovery of chlorine from liquefaction tail gas. Results suggest the following:

- (1) Service in chlorine is more onerous than the typical membrane gas-separation process. The key challenge is the selection of a membrane which is selective for chlorine, chemically resistant, and serviceable at the low temperatures characteristic of chlorine recovery processes. Many polymers degrade rapidly upon exposure to chlorine, and glassy polymers are not likely to have suitable physical properties. The three candidates identified in screening tests were silicone rubber, EPM and EPDM. Of these, silicone rubber had the highest selectivity for chlorine and performed well in exposure tests in gas mixtures and in pure chlorine. In laboratory tests, the preferred membrane showed chlorine/nitrogen selectivities ranging from 40 to more than 100. All results and calculations reported in this chapter are based on silicone rubber membranes.
- (2) The membrane selectively rejects oxygen and nitrogen. The field test showed a selectivity for chlorine over nitrogen of about ten. That this is so much lower than that obtained in the laboratory is attributed to concentration polarisation. Increasing the rate of flow through the module can alleviate this. At the same time, chlorine recovery can be maintained by adding modules in series. This is precisely what would be done in a commercial unit, and so one can reasonably expect better results in full-scale operation.
- (3) Hydrogen is also selectively rejected, although not so strongly as nitrogen. In a plant running close to the lower explosive limit of 4% hydrogen, any partitioning can cause the exit streams of one of the membranes to move into the explosive range. This must be considered in design, and particularly in some non-membrane cell operations it will be necessary to add more diluent gas to the process. The low permeability of hydrogen means that with typical chlorine plant gas compositions it will accumulate in the reject. When the recovery of chlorine is quite high, the fact that hydrogen permeates more readily than nitrogen can reverse the situation. The concentration of hydrogen in the combined permeate may reach a maximum inside the permeators.
- (4) Carbon dioxide permeates the membranes at least as readily as does chlorine. This fact will produce a significant increase in CO_2 concentration in a recycle system. For best results at highest chlorine recovery, it will pay to keep the CO_2 concentration in the membrane feed-gas low. This can be accomplished in most plants by acidification of cell-feed brine. Acidification is highly recommended in any case when a very high degree of chlorine recovery is required, whether by

liquefaction alone or by liquefaction supplemented with membrane separation. The CO_2 problem is one to be solved before, not after, the cells.

- (5) The heat of permeation of chlorine in a silicone rubber membrane is -3 to -5 kcal mol^{-1} while that of nitrogen is 1.0 – $1.5 \text{ kcal mol}^{-1}$. Separation of these gases therefore is helped by low temperature. The flux of chlorine actually increases as temperature is lowered, reflecting the increased sorption. The flux of nitrogen decreases, reflecting the lower diffusivity.
- (6) Selectivity and the normalised flux ($J/\Delta p$) of chlorine are lower at high pressures or concentrations. This may be a result of increased plasticisation.

Applying this information to a typical diaphragm-cell tail gas, Fig. 7.4 shows the logarithm of the amount of unrecovered chlorine versus the relative membrane area required. Recovery of chlorine is not far from a first-order process. As chlorine selectively passes through the membrane, the partial pressures of the impurities increase in the remaining gas. This causes their rates of permeation to increase. The membrane area required for permeation of, say, 30% of the nitrogen is less than twice that required for 15%.

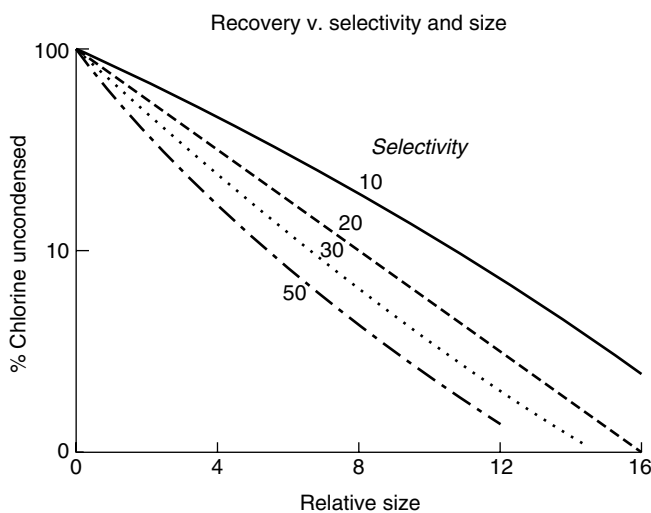


Fig 7.4 Chlorine recovery versus selectivity and size.

The concentration of chlorine in the total permeate continuously decreases as the process continues. This is illustrated by Fig. 7.5, showing the percentage of the nitrogen originally present which accompanies permeation of 80% and 90% of the chlorine. The purity of the gas is a measure of its utility in further processing. One option is to recycle the permeate to the liquefaction process. This is discussed in more detail in Section 7.3.3.

Only the lowest selectivity used in Figs 7.4 and 7.5 has been demonstrated on a

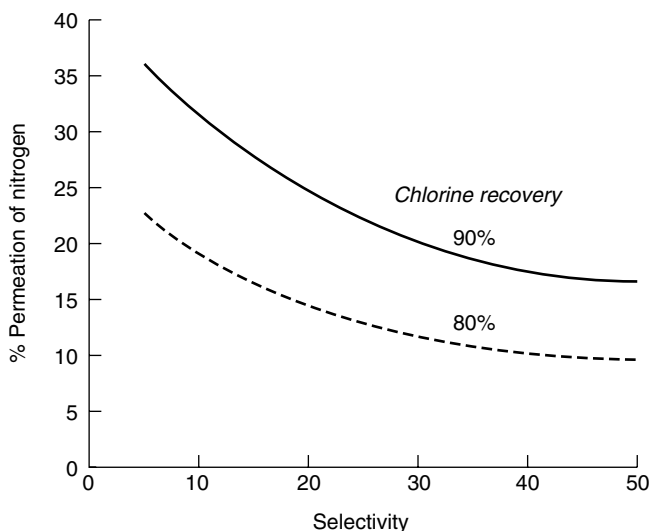


Fig 7.5 Nitrogen permeation as a function of chlorine recovery.

large scale. The others, however, are all within the performance seen in the laboratory. Perhaps some of the difference is due to inadequacies in the model used for calculation, in which it is assumed that selectivity is constant and that there is perfect cross-flow along the length of a module with no back-mixing on either side. More probably, the known effect of concentration polarisation is being observed. This was alluded to above, and its relief in scaled-up units was explained. While the use of the higher selectivities may seem speculative then, it is a highly reasonable speculation.

7.3.3 Membranes as adjuncts to liquefaction

Next, ways to augment liquefaction and bring chlorine recovery to more than 99% are considered. To eliminate some of the many variables, only the off-gas from a two-stage liquefier, as in Fig. 7.2, condensing 97.7% of the chlorine from a membrane-cell installation is utilised. The gas is available at 800 kPa.

The conventional approach is to add a third stage of liquefaction, in this case operating at lower temperature. Lower temperatures recover more chlorine at the expense of higher energy consumption and a more costly installation. An alternative is to install a bank of permeators and recycle the permeate to the first stage of liquefaction, as in Fig. 7.6. The need for low-temperature liquefaction disappears, but energy is expended by recompressing the permeate. The flows through the liquefaction section, and the demands on its equipment, also increase.

Figure 7.7 (to be read alongside Table 7.1) shows that there is little to choose between the two schemes in their overall energy requirements. Advantages accrue to the membrane approach at very high degrees of recovery because of the very low temperatures (-80°C and below) required for liquefaction. Not only is operation more difficult and more energy intensive, but the refrigeration plant is becoming a

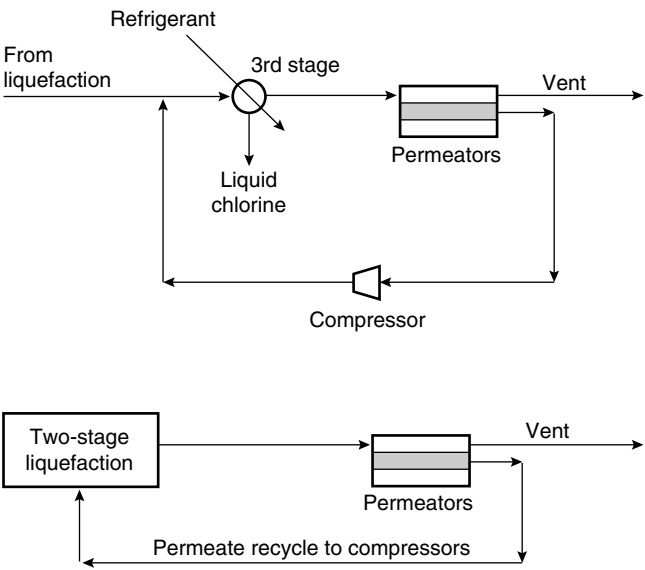


Fig 7.6 Liquefaction process augmented with membranes.

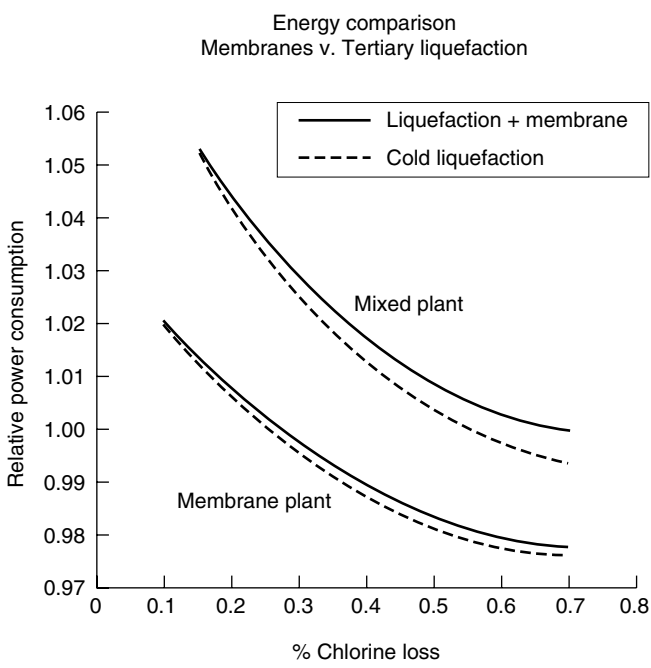


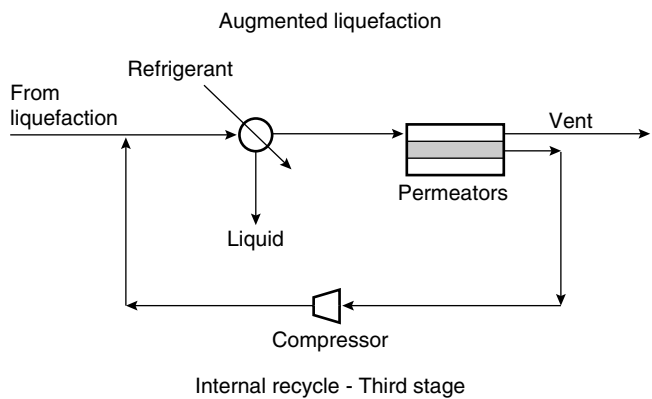
Fig 7.7 Relative power consumption: membrane addition versus cold liquefaction.

speciality item. In a retrofit project, the balance swings against the membrane process. What can be achieved without great expense will be limited by the capacity of the existing compression/liquefaction plant.

Figure 7.8 shows a different approach that combines the two schemes. A third stage of liquefaction is added, and its off-gas is sent to a group of permeators. The permeate

Table 7.1 Comparison of numerical data obtained from Fig. 7.7.

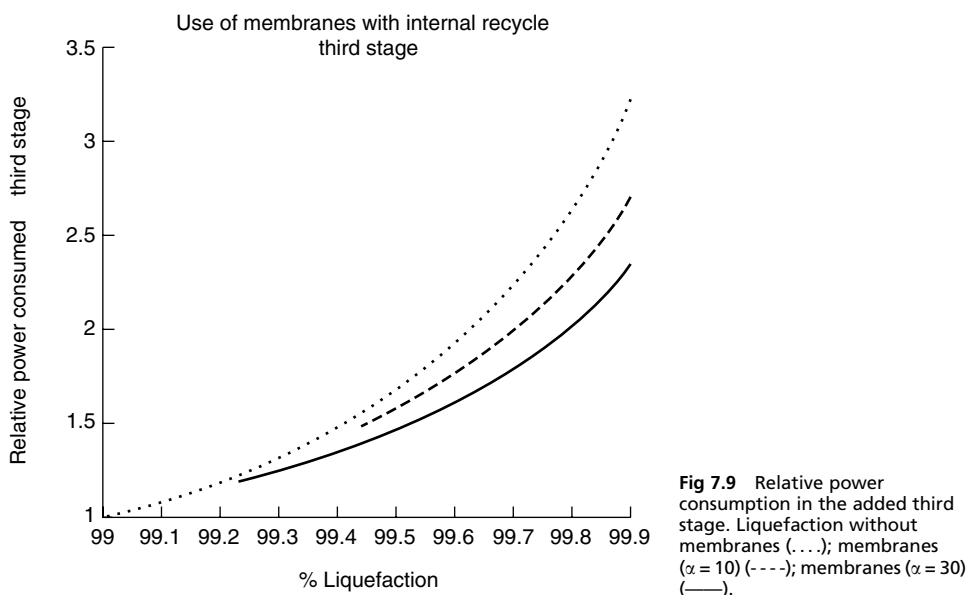
Chlorine loss (%)	Mixed plant		Membrane plant	
	Liqfn. + Memb.	Cold liqfn.	Liqfn. + Memb.	Cold liqfn.
0.1	—	—	1.0205	1.02
0.15	1.0537	1.0535	1.014	1.0128
0.2	1.0448	1.0435	1.0081	1.0065
0.25	1.0367	1.0343	1.00275	1.0009
0.3	1.0295	1.0261	0.9979	0.9958
0.4	1.0173	1.0125	0.9897	0.9876
0.5	1.0084	1.0027	0.9836	0.9817
0.6	1.0026	0.9966	0.9795	0.9782
0.7	1.0000	0.9942	0.9775	0.9761

**Fig 7.8** Augmented liquefaction: combination process.

is compressed for recycle to the third stage only. This is feasible in a retrofit as well as in a Greenfield project. The third stage operates at conventional temperatures even at very high degrees of recovery. The process gas-flow through the liquefier increases and the refrigeration load goes up slightly. The energy required to generate a tonne of refrigeration, however, remains nearly constant. Figure 7.9 shows that at high degrees of liquefaction the installation of membranes reduces the energy consumption of this stage by up to 40%. With all the chlorine condensed at -40°C , moreover, the concentration of dissolved inerts is lower. Table 7.2 shows results between 99.5 and 99.9% overall recovery.

7.3.4 Chlorine as raw material for vinyl chloride

Elsewhere in this book, White and Sandel [7] discuss the integration of chlorine and ethylene dichloride (EDC) processes. The oxygen content of the chlorine fed to an EDC unit must be kept within the process specification. This can be achieved by liquefying at least part of the chlorine in order to reject non-condensables or by acidifying the brine fed to the cells. Oxygen results from the anodic oxidation of hydroxide ions; free acid in the feed brine will neutralise those ions and so reduce the amount of oxygen formed.

**Table 7.2** Reduction of dissolved inerts: concentration by combination process.

Recovery (%)	Wt.% dissolved inerts, third stage	
	Low-temperature liquefaction	Liquefaction plus membranes
99.5	0.9	0.7
99.8	2.0	0.8
99.9	3.6	0.9

When a cell line has been in operation for some time, there will be a range of current efficiencies reflecting different degrees of damage suffered by the individual membranes. More heavily damaged cells will tend to produce more oxygen, and these cells will require correspondingly more acid addition to restore gas purity. However, the best cells often limit the amount of acid that can be added. If a group of cells is fed brine at a pH appropriate to the worst cells, the excess acid in the best cells may be sufficient to protonate the membranes, converting the useful alkali carboxylate sites to the non-conductive $-\text{COOH}$. This problem is avoided only by reducing the flow of acid and so feeding an insufficient amount to the less efficient cells.

This danger to the membranes, as well as the potential for localised corrosion of titanium, has been a great obstacle to production of low-oxygen gas in membrane cells. The difficulties can be overcome to a great extent by providing multiple addition points for acid and by ensuring that the brine entering the cells is rapidly and efficiently dispersed. The latest generation of electrolyzers is designed specifically to operate at higher current densities than had been practicable in the past and to produce cell gases with oxygen contents as low as 0.5% [8–10].

Here we consider gas-separation membranes as an alternative or adjunct to these

designs. Figure 7.10 (to be read alongside Table 7.3) shows how much chlorine can be recovered with an oxygen content of no more than 0.7%. This is higher than the 0.5% referred to above. It allows for, over time, less than optimum performance of the cells, and it is near the middle of the desirable range quoted by White and Sandel [7]. The operating pressure is limited to 345 kPa. This keeps the maximum partial pressure of chlorine close to the levels already tested with silicone rubber.

As the oxygen content in the process gas increases, the amount recoverable decreases. Based on the field test already quoted, it would be impossible to produce a useful amount of low-oxygen gas from a feed-gas containing more than about 2% oxygen. If the feed-gas were purer or the operating pressure higher, more could be

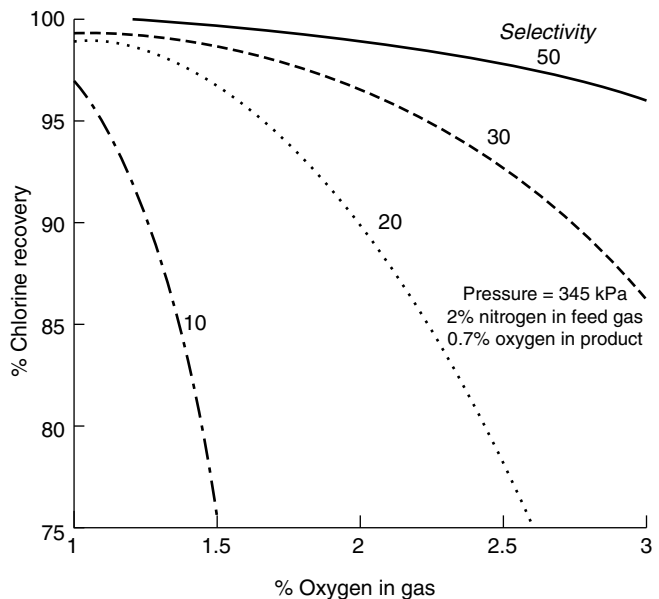


Fig 7.10 Recovery of EDC feedstock from cell gas.

Table 7.3 Recovery of chlorine from cell gas with an oxygen content of no more than 0.7%. Data obtained from Fig. 7.10.

Chlorine recovery (%) at given selectivity of Cl_2 over N_2				
O_2 content (%)	10	20	30	50
1	96.8	99.15	99.56	—
1.1	95.2	98.94	99.53	—
1.2	92.3	98.77	99.5	99.8
1.4	82.5	97.63	99.15	99.7
4.5	75.5	96.77	98.82	99.6
1.6	—	95.73	98.52	99.5
1.8	—	93.08	97.6	99.2
2	—	89.66	69.39	98.9
2.3	—	83.12	94.04	98.2
2.6	—	75	91.04	97.4
3	—	—	86	96

recovered. Using laboratory results, much higher recoveries are possible from gases containing 2% or 3% oxygen. The examples in this chapter assume a selectivity for oxygen over nitrogen of about 2.2. The ‘selectivity’ referred to in Fig. 7.10, to be consistent with the rest of the chapter, is that of chlorine over nitrogen.

The use of membranes for this separation provides the EDC producer with an additional degree of freedom. Higher oxygen contents can be accepted in the cell gas. The cost of a membrane installation can be offset by the cost of upgrading or replacing electrolyzers or by the capital and operating cost of providing many connections for additions of acid to the brine.

This is an area that may reward further work with membranes.

7.4 Economics

Lokhandwala *et al.* [6] have already provided costs for the membrane-based upgrading of tail gas for recycle to a liquefaction process. They showed that recovery of 228 kg h⁻¹ (1915 tonnes per annum) of chlorine from a 20% (v/v) tail gas should provide a pay-out time of about 14 months. Other comparisons made by Membrane Technology and Research, Inc. [11] for an 800 tonnes per day plant shown in Table 7.4 give similar results.

Table 7.4 Incremental recovery of chlorine by membranes (800 tonnes day⁻¹ plant; liquefaction conditions – 18°C and 450 kPa).

Inerts in gas (%)	Liquefied (%)	Recovery with membranes (%)	Value of chlorine recovered (\$m per year)	Installed cost of membranes (\$m)
3.0	97.5	99.5	578	450
4.9	95.6	99.1	994	700

The value of the extra chlorine recovered will pay for the membranes in about nine months. Addition of operating costs still gives an attractive pay-out. However, the base case for Table 7.4 assumes that nothing is done to handle the chlorine issuing from liquefaction. This is not an option. The real question is how the membrane process compares with the alternatives, and this is the subject of Table 7.5. The basis assumed is an 800 tonnes per day plant with gas composition 93.16% Cl₂, 2.40% O₂, 3.82% N₂, 0.37% CO₂, and 0.25% H₂. The table covers costs only. Product values are highly sensitive to local conditions and are not included. In all cases, the membrane option is based on the field test in order to give the most reliable numbers available. Technological development will improve the case for the use of membranes.

Production of HCl has certain advantages in operating costs. These amount to approximately \$100 000 per year, or to \$17 per tonne of chlorine content. Much of the difference is due to the conservative assumption of a membrane life of one year. If membranes lasted two years, the difference would almost disappear. An

Table 7.5 Comparison of costs of tail-gas recovery methods based on field tests of membranes (16 tonnes day⁻¹ chlorine available at 690 kPa).

Process	Capital cost (\$m)	Raw material cost (\$m per year)	Other operating costs (\$m per year)	Total cost ^a (\$m per year)
Membrane recovery	700	60	200	400
HCl production	800	80	65	305
NaOCl production	500	1150	30	1300
Tertiary liquefaction	900	60	175	415

^a Capital charge of 20% per year.

important consideration not addressed in a simple cost comparison is the quality of the 'market' for the product. Enhanced recovery of chlorine has no marketing drawbacks; its value, at a minimum, is the avoided cost of generating and processing additional gas. Recovered by-products, such as hydrochloric acid, may not be reliably marketable at a good price in small quantities tied to the production of another item. Selling HCl at a reduced price or adding large storage facilities and a sales effort would soon eliminate the apparent advantages of its production. If all the HCl can be consumed on-site, on the other hand, this approach is secure and is most often the best alternative.

Table 7.5 also considers the production of NaOCl bleach. While any chlorine production process must have an emergency vent scrubber system, and while most of these produce quantities of NaOCl, some adaptations may be necessary to allow steady production of full-strength high-quality bleach. Separate product storage and shipping facilities would also be necessary. The major cost is the assigned value of the NaOH consumed in this process. Following Lokhandwala *et al.* [6], NaOH is charged at \$180 per tonne. In this case, the cost advantage is with the membrane process, to the tune of about \$160 per tonne of chlorine. The bleach market would have to be reliable and provide at least that much differential netback to justify this approach.

The last entry in Table 7.5 allows comparison of membrane processing with an expanded liquefaction system. There is little to choose between the two. However, to match the recovery obtained by the membranes required very low liquefaction temperatures.

7.5 Conclusion

Gas-separation membranes offer a promising alternative for chlorine processing. Results obtained so far in field tests are not outstanding, but we have seen that there are sound technological reasons to expect better performance in a true commercial installation. Little has yet been done to tailor membranes to the recovery of chlorine. Given that fact, perhaps regard should be paid to those already tested and reflect on the progress that has been made there as the equivalent test tests lots of early unmodified sulphonate ion-exchange membranes.

Acknowledgements

Kaaeid Lokhandwala of Membrane Technology and Research, Inc., Menlo Park, California provided guidance and the results of calculations for several cases, which served as the model for all other calculations reported here. Kathleen Jelliffe provided graphics for the oral presentation of this chapter.

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Chapter 8

Electrode Management Optimisation System

G Tremblay and S Harrison

8.1 Introduction

The Electrode Management and Optimisation System, known as EMOSTM, is an intelligent system. Such systems are designed to emulate and enhance human capability to perceive, reason, take decisions and act in a complex environment. They typically use such tools as expert systems, neural networks and fuzzy logic. Over the past ten years the maturity of these systems has been made possible by the rapid advancement of computational power combined with progress made in the field of artificial intelligence (AI). There has been a growing movement in the past few years in the industrial sector to implement intelligent systems in industries such as energy, health and telecommunications. Intelligent systems in process control make use of expert systems and neural networks not only to monitor operations, but also to diagnose problems and optimise operations.

The main objective for an intelligent system in electrolyser operations is to gather and process valuable information for a greater control and efficiency. To achieve the aforementioned objective, two key functions have to be performed properly. Firstly, accurate and precise real-time data need to be obtained; and secondly, the system should be able to process and interpret these data based on fundamental and acquired industrial electrochemical knowledge. In the case of R2's EMOSTM, this second key element refers directly to its capability to use embedded human expertise to find optimal operating solutions and to detect and correctly identify equipment degradation or other anomalies.

8.2 EMOSTM

EMOSTM is a combined hardware and software system that gathers chemical and electrical parameters in real-time and processes them so that close process monitoring is maintained along with information that will lead to process optimisation (see Fig. 8.1). EMOSTM is composed of three main components:

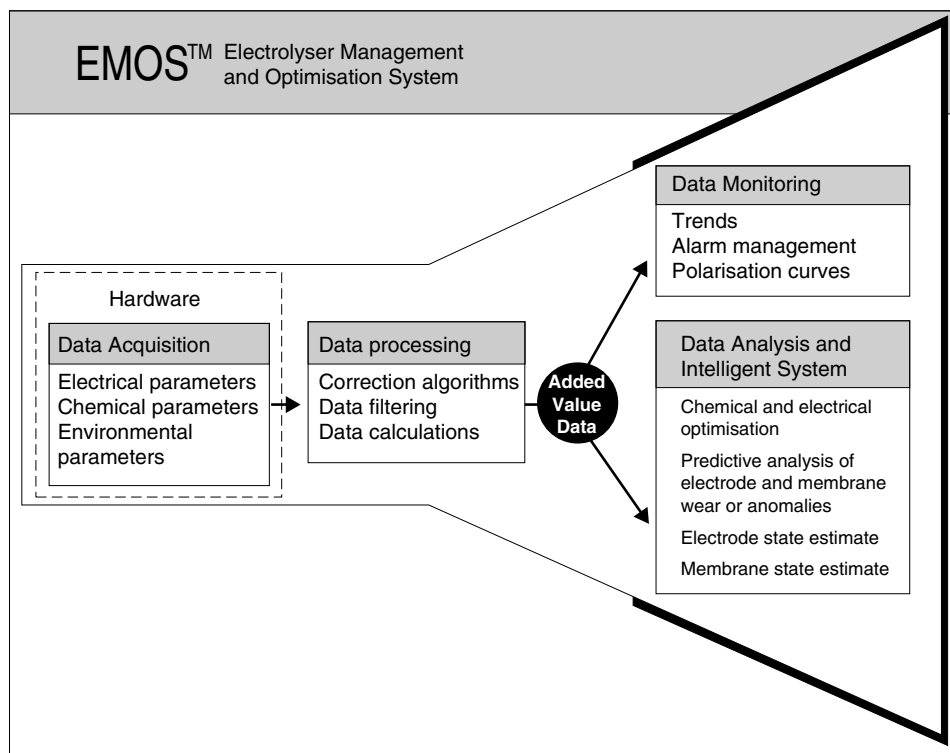


Fig. 8.1 Schematic overview of the EMOS™ system.

- (1) data acquisition based on a unique hardware to obtain precise cell and other voltages, as well as typical process and chemical data;
- (2) data processing to produce so-called value-added data, involving filtering to remove background interference and algorithms to correct and correlate the data obtained from different sources; and
- (3) the processed data are then stored and used in process monitoring and by the intelligent system.

8.2.1 The hardware and data acquisition

The acquisition of precise data is critical, as it is the foundation of subsequent calculations and analysis that are used by an intelligent system such as EMOS™.

Precise electrical data acquisition within the industrial electrolytic plant typical of chlorate and chlor-alkali production facilities represents a significant challenge as the precision of the data obtained is usually degraded in an environment characterised by electrical noise induced by rectifiers and by strong electromagnetic fields. In some cases, rectifier-induced noise such as harmonics and switching peaks in the order of

600 mV have been observed. EMOS™ hardware has been specifically designed to address these concerns and with, of course, a reliability factor that is consequent with extensive use in a hostile environment (see Fig. 8.2). Until recently this kind of environment has been a major obstacle to obtaining precise data.

The EMOS™ hardware is capable of measuring cell and electrolyser voltages with the following typical characteristics:

- ± 0.0025 V accuracy for individual electrode readings
- reliability due to extensive field-testing
- complete electrical insulation
- use of fibre optics
- immunity to hostile environments

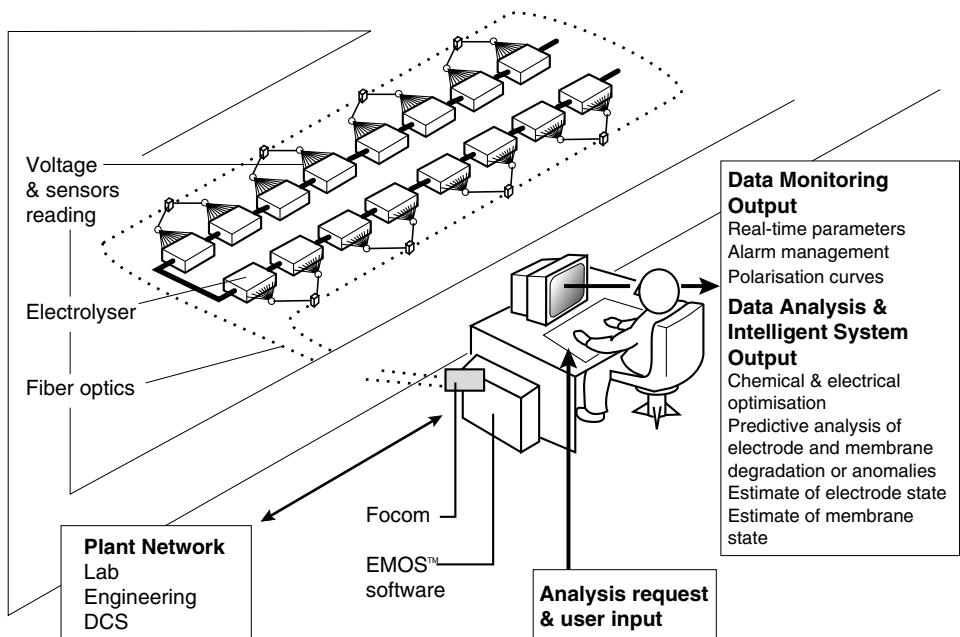


Fig. 8.2 Schematic representation of an EMOS™ installation.

Electrical voltage data from individual cells and electrolysers are collected, filtered and converted to digital signals as close as possible to the source to preserve accuracy using an array of distributed acquisition modules (MODA). A fibre-optic network transports the data, in its digital form, to the main computer for processing. This method of transport retains a quality of data, as electromagnetic fields have no effect on signals transported by fibre optics. The entire set-up is completely insulated electrically and it is powered directly from the line's current; therefore it does not

require an additional power supply. Other data can be directly acquired from the plant's laboratory, from the on-site DCS or from direct user input where required. The system is fully scalable and can be adapted to the needs of the user so additional data points can be added depending on the electrolysis technology.

The data acquisition system allows EMOS™ to generate polarisation curves during periodic changes in current and voltage and during start-up and shutdown of the electrolysis cell. The polarisation data are obtained in point form as shown in Fig. 8.3 and then converted into curves as shown in Fig. 8.4. The polarisation curve data need to be corrected for changes in temperature and electrolyte composition before the results can be useful. The typical information that is obtained directly or indirectly by the EMOS™ is provided in Table 8.1.

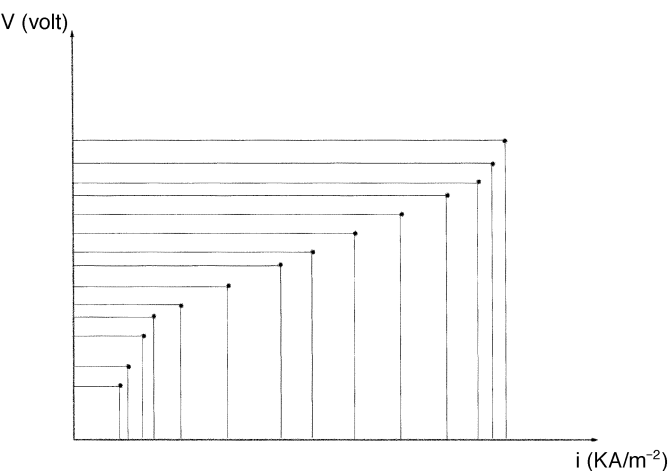


Fig. 8.3 Synchronised voltage–current data for polarisation curves.

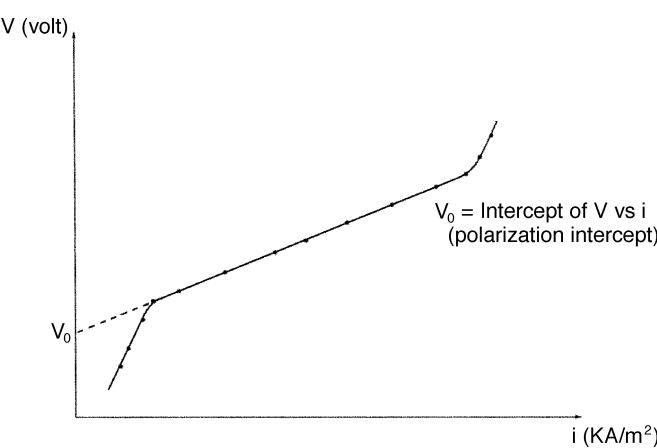


Fig. 8.4 A typical polarisation curve.

Table 8.1 Typical information obtained by EMOS™.

Acquisition and input	Value-added data
Cell electrolyser voltage	Normalised voltage
Line current	Differential voltage
Temperature	Temperature-corrected voltage
Chemical analysis parameters	pH-corrected voltage
Electrolyte conductivities	Polarisation curve
Sodium balance	Historical database
pH	
Acidity	
Other plant analyses	

8.2.2 Data analysis and intelligent system

The data analysis and intelligent system components of EMOS™ process the acquired data as well as value-added data using several software modules or engines including:

- pattern recognition
- polarisation curve
- predictive module
- optimisation engine

as well as in the expert system which interacts with the aforementioned modules to act as the intelligent system. The knowledge-base embedded in the expert system comprises the fundamental electrochemical knowledge such as the decomposition voltage, anode and cathode overpotentials, the electrolyte and membrane conductivities as well as the influence of temperature on these basic parameters. The model that is the basis of the intelligent system is derived from the following standard equation:

$$V_{\text{cell}} = V_D + |\eta_c| + |\eta_a| + iR_a + iR_c + iR_m \quad (8.1)$$

where V_D is the decomposition voltage, η_c and η_a are the cathodic and anodic overpotentials, respectively, and iR_a , iR_c and iR_m are the resistive losses in the system for the anolyte, catholyte and the membrane, respectively. The decomposition voltage is well known and can be derived from equations available in the literature [1], including relationships related to temperature and electrolyte composition. The cathodic and anodic overpotentials are functions of the anode and cathode materials being used and therefore they are typical of the components being used.

The fundamental model is supplemented by the knowledge and expertise of the operators and engineers operating the plant as well as information typical of the cell design. As can be seen in Fig. 8.5 the intelligent system is interactive between the expert system and the other modules of the intelligent system. Once the intelligent system has learnt the fundamental and specialised knowledge that comprises

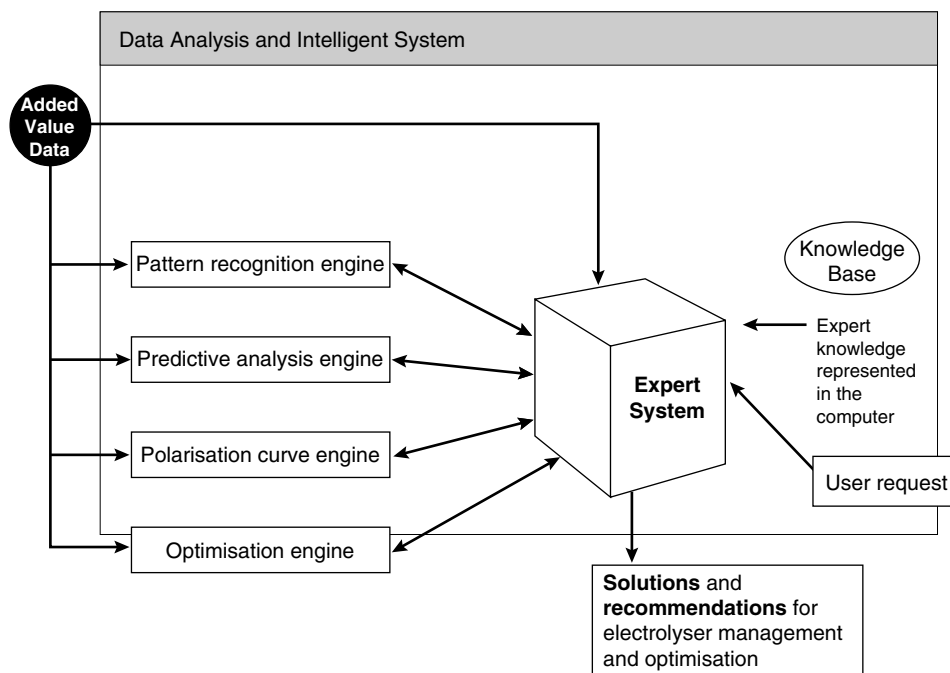


Fig. 8.5 Interaction between the expert system and the other modules of the intelligent system.

the expert knowledge it can be used to suggest solutions and make recommendations in the operation of the electrolyzers and cell lines both with respect to applied current and local electrolyte composition. In the chlor-alkali context this could mean modifying the electrolyte composition as a function of the state of membranes in a cell line.

8.3 Applications and methods

8.3.1 Electrode management

In the manufacture of sodium chlorate, the EMOSTM system has been employed to alter a process where all electrodes are usually replaced after just several years of operation and where it is known that typical lifetimes of anodes are between five and ten years. Owing to the monitoring capabilities of EMOSTM it is now possible to change only those anodes that are known to be poorly performing rather than all electrodes. This is achieved by monitoring closely individual cell voltages by employing the expertise of plant engineers and using the polarisation module to indicate which electrodes require changing. This aspect of EMOSTM is very impor-

tant as anode coating is a significant cost to the process and thus, if the coating of the majority of the anodes can be delayed for one or two years then significant savings can be made, albeit potentially at the cost of some additional shutdowns. If, however, the electrolyser is properly managed then the additional shutdowns for anode changes can occur at the same time as other routine maintenance. EMOSTM has also been used to determine when electrodes are poorly coated or malfunctioning on installation, thus saving operators significant costs in re-coating faulty electrodes.

8.3.2 Electrolyte composition

As anodes age their performance gradually deteriorates, and thus small changes in electrolyte composition must be made to maintain current efficiency and energy consumption. The EMOSTM system has been used by some operators to determine the optimum composition of the electrolyte in these circumstances and in some cases to control the composition selectively for each cell line.

8.3.3 State of the electrodes

In chlorate production the EMOSTM system has also been used to determine the formation of deposits on the electrodes, either the anode or cathode and combined with the information on process and electrolyte composition the system determines the need for cell cleaning or acid rinsing. The close monitoring of individual cell voltages has allowed plant engineers to establish the most appropriate current density for production lines dependent upon the state of the anode coatings. This allows for the same overall production capacity while permitting the operation of two different cell lines in the cell room at different current densities based upon the state of the anodes and cathodes in the cell.

8.3.4 Safety

The close monitoring of electrolyser and cell voltages allows operators to observe small changes in cell voltages. By using pattern recognition to determine known trends in the cell voltage that can be or are known to be dangerous, it is possible to store information in the database of the computer-based expert system. One example of the use of pattern recognition has allowed one operator to eliminate completely a potentially explosive situation. Previously such an incident was only observable a few seconds before the explosion occurred in the electrolyser. Through EMOSTM the indications of such an incident are observable weeks in advance and the explosion averted by shutting down the cell in a controlled fashion. This is a major example of the use of EMOSTM in routine safety.

8.3.5 Chlor-alkali

In chlor-alkali production, EMOSTM should be able to determine problems with both anode coatings and membranes. The literature is replete with examples of the effect of different impurities on membranes [2] and of the analysis of different problems using polarisation curves to determine their cause [3, 4]. These analysis techniques have been incorporated into the expert system in the form of approximations of the polarisation curves. Use is made of the familiar k-factor (see Equation 8.2) or the more accurate logarithmic form of this factor (Equation 8.3):

$$U = C + ki \quad (8.2)$$

$$V_t = S \times \log(I) + R \times (I) + Q \quad (8.3)$$

where S is derived from the composite Tafel slope given by $B_a + B_c$, R is the composite resistance equal to $R_e + R_s + R_b$, and Q is equal to the sum of constants $A_a + A_c + E_a + E_c$.

A more detailed explanation of these equations can be found in Hardee [4]. The close monitoring of cell voltages is expected to enable operators to observe problems with membrane blistering and potentially dangerous situations such as membrane tears before they become dangerous or explosive.

8.4 Conclusion

EMOSTM has to date been mostly used in chlorate manufacture, but R2 in Montreal, Canada has recently installed its system on an FM-21 1500-type cell chlor-alkali production facility. This is presently a pilot installation, with only six cells currently being monitored. This installation has led to the monitoring of cell currents rather than cell voltages owing to the monopolar design of these electrolyzers. It is too soon to make detailed conclusions about this installation as it has only been fully operational since January 2000.

In the chlorate industry, EMOSTM has proven its utility and cost-effectiveness in several production units throughout North America. It has been developed from an industrial perspective based on a flexible modular system and has demonstrated good reliability with over five years of continuous operation in some chlorate facilities. The system can be installed inside a few days requiring minimal shutdown of production facilities. Its operation is simple and non-intrusive on the normal control of the electrolyser process.

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Chapter 9

Gas-diffusion Electrodes for Chlorine-related (Production) Technologies

F Federico, G N Martelli and D Pinter

9.1 Introduction

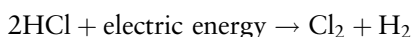
The industrial production of chlorine is today essentially achieved through sodium chloride electrolysis, with only a minor quantity coming from hydrochloric acid electrolysis. Further substantial improvements in energy consumption are no longer obtainable with conventional technology involving the generation of hydrogen at the cathode. In fact, it can be stated that at present the best cell designs have pushed to extreme limits the catalytic activity of electrodes, the conductivity and selectivity of membranes, and the electrical, mechanical and hydraulic effectiveness of the hardware employed.

In contrast, the scope of improvements may be easily widened with the incorporation of oxygen-consuming gas-diffusion electrodes (GDE) in the construction of electrolyzers as a substitute for the conventional hydrogen-evolving cathodes.

This chapter describes the improvements made to the GDE of the prior art (which was industrially unattractive) resulting in the present-day GDE characterised by very positive properties and behaviour not only in laboratory cells, but also in demonstration electrolyzers on an industrial scale. (This subject is discussed in a separate chapter of this book.)

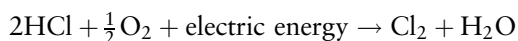
9.2 Oxygen-depolarised cathode for aqueous hydrochloric acid electrolysis

In conventional hydrochloric acid electrolysis [1], aqueous hydrochloric acid (HCl_{aq}) is electrolysed in a cell, constructed basically from graphite, which is divided by a porous diaphragm or a membrane. The overall reaction is



with a typical power consumption of about 1500 kWh per tonne of Cl_2 .

The substitution of the traditional cathode with an oxygen-consuming GDE involves a new overall reaction, which may be written as



with a theoretical energy saving of about 700 kWh per tonne of Cl_2 .

Early examples of the industrial application of this process (e.g. in the 1970s, General Electric [2] used first-generation ion-exchange membranes and SPE® technologies) were not successful, mainly because of stability and activity/performance problems with the GDE.

9.2.1 Stability

Platinum is generally acknowledged as the most effective catalyst for the electro-reduction of oxygen in a wide range of conditions (e.g. fuel cells). In the instance of aqueous HCl electrolysis, the basic drawback is corrosion or deactivation of the catalyst during cell shutdown, owing to chemical attack from HCl and chlorine that diffuse across the membrane.

This problem can be solved partially with careful procedures for cell shutdown, including use of a polarisation current (about 50 A m^{-2}) and flushing of the cathode chamber with nitrogen. In these conditions the cathode works as a hydrogen-evolving electrode at the potential required for protection from chemical attack. This solution, however, requires additional costs, and appears to be rather critical in view of the long lifetime required for industrial application of catalysts.

A real breakthrough towards the reliable industrial application of a catalyst is represented by the development of a new rhodium (Rh)-based catalyst, manufactured by the E-Tek division [3] of DeNora North America. This has demonstrated an ability to overcome substantially the above-mentioned problems of chemical attack.

Initial tests run with small laboratory cells (6.45 cm^2) demonstrated excellent stability during uncontrolled shutdown conditions (Figs 9.1 and 9.2). The evaluation

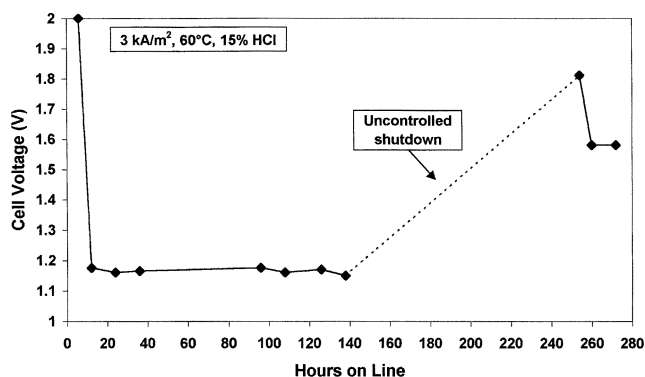


Fig. 9.1 Typical shutdown result for a laboratory HCl_{aq} cell (6.5 cm^2) with platinum catalyst.

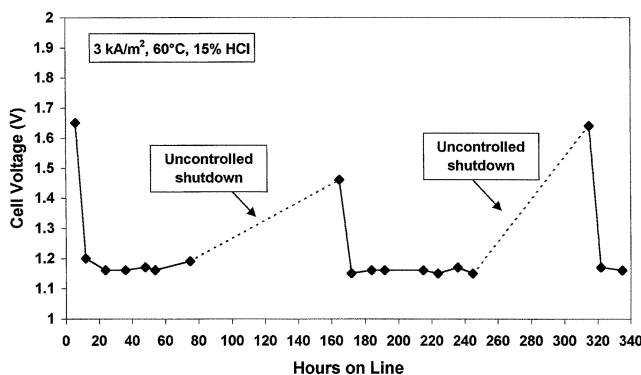


Fig. 9.2 Typical shutdown result for a laboratory HCl_{aq} cell (6.5 cm^2) with rhodium catalyst.

of the catalyst was then moved to 1 dm^2 laboratory cells (at both the DeNora Milano and Bayer Leverkusen laboratories), with the same encouraging results (Figs 9.3 and 9.4). Finally, four Rh-based electrodes (0.88 m^2 each) were installed in a pilot electrolyser plant at the Leverkusen laboratory. These electrodes have now totalled nine months of operation without any indication of a noticeable deterioration of performance, even after many uncontrolled shutdowns and use of a technical grade HCl_{aq} feed (Fig. 9.5).

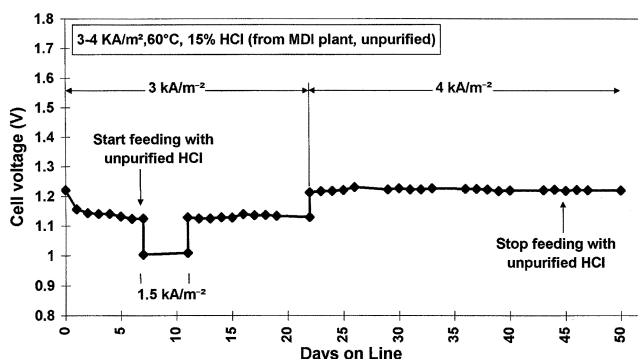


Fig. 9.3 An unpurified MDI-type HCl feed test of a laboratory cell (1 dm^2) with a rhodium-based oxygen-depolarised cathode.

9.2.2 Activity/performances

With GDE cathodes (whether Pt- or Rh-based) the energy saving is not as large as expected from the thermodynamics.

The GDE cathode, when incorporated into a membrane fuel cell, is characterised by a potential in the range of $0.6\text{--}0.7 \text{ V}$ (NHE). On this basis, the expected cell voltage for the oxygen-depolarised HCl_{aq} electrolysis should be around 0.8 V . In reality the measured cell voltage at 4 kA m^{-2} is in the range of $1.2\text{--}1.3 \text{ V}$. If it is assumed that the deviation from the expected value is totally due to the cathode, one can conclude that the cathode potential has dropped down to $0\text{--}0.1 \text{ V}$ (NHE). Figure 9.6 shows the voltage–current relationship for an HCl_{aq} cell. What is the reason for this behaviour?

Fig. 9.4 Feed test of a laboratory HCl_{aq} cell (1 dm^2) with a rhodium-based oxygen-depolarised cathode.

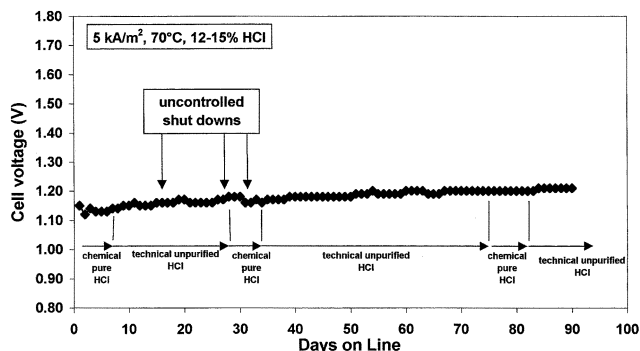


Fig. 9.5 Cell voltage results of an HCl_{aq} pilot electrolyser (four cells, 0.88 m^2 each) with rhodium-based oxygen-depolarised cathodes.

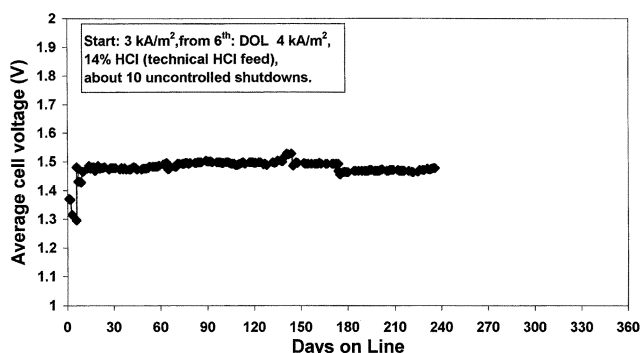
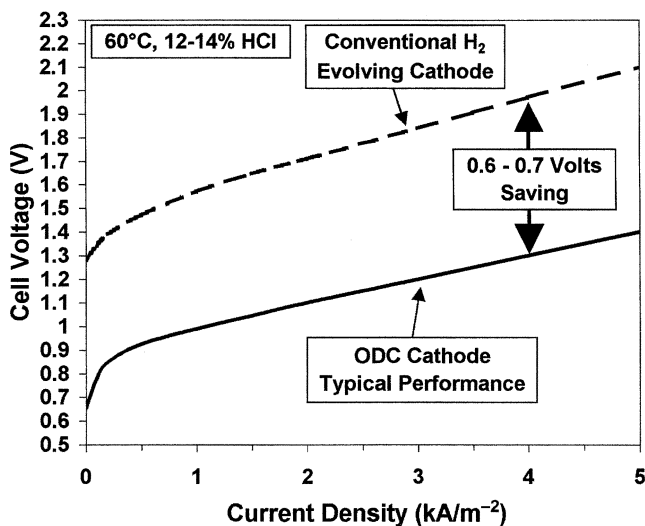


Fig. 9.6 Voltage-current results of HCl_{aq} electrolysis with a rhodium-based oxygen-depolarised cathode.



The explanation is in some part associated with a quantity of HCl permeating through the membrane and forming, during cell operation, an acidic chloride-containing cathode condensate. It is well known that chloride ions act as a poison for the oxygen-reduction reaction. A second consideration is derived from the structure of the GDE. Since the cell operates at a maximum temperature of 60°C, the water formed by the reaction and diffusing across the membrane is present as liquid. This is contrary to what happens at a membrane fuel cell cathode, where the reaction layer operates at about 80°C and the water produced is removed as steam.

The GDE for hydrochloric acid electrolysis is characterised by micro-scale 'hydraulic' problems connected with the competition between the gas phase (oxygen), which has to diffuse towards the catalyst, and the liquid phase (water), which must be released. This competition is managed basically by a flow-through structure provided with hydrophobic channels of relatively large diameter. These are formed from PTFE (the binder of the structure) and catalyst particles and account for regulating the gas phase. Hydrophilic channels with smaller diameters (one order of magnitude smaller), which are located in the micro-porous carbon particles of the catalyst support (e.g. Vulcan XC-72), act as water absorbers. A consequence of the electrolysis process is that the catalyst itself is partially covered by liquid. This reduces its effectiveness and accounts for extra voltage.

The flow-through cathode is the result of a tailored-to-the-process evolution of the GDE structure, which is available also in two additional configurations: double-sided (originally developed for fuel cell servicing) and single-sided (see Fig. 9.7). The double-sided type is particularly suited for the electrochemical process where the product should not be released on to the back surface of the cathode, as in the case of oxygen-depolarised chlor-alkali electrolysis, discussed in Section 9.3.

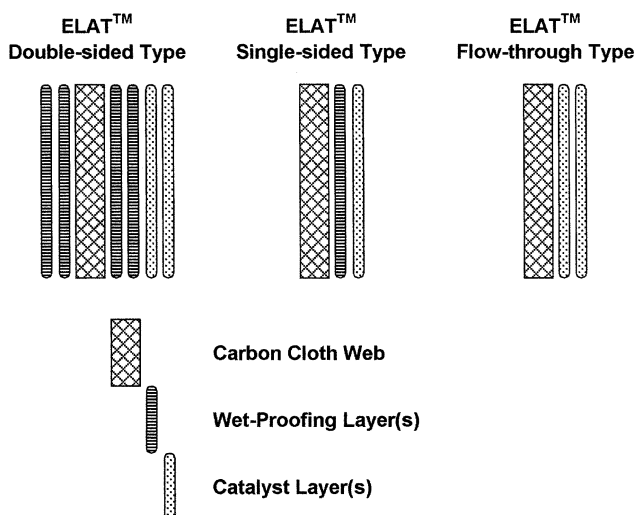


Fig. 9.7 Various gas-diffusion electrode (GDE) design structures.

9.2.3 GDE assembly in the cell

The presence of HCl_{aq} in the interior of the GDE leads to certain drawbacks, as discussed in Section 9.2.2. These are represented basically by an increase of the overvoltage, i.e. an increase of cell voltage. In contrast, however, the conductive liquid phase plays a positive role, as the transfer of protons from the membrane to the catalytic particles is strongly facilitated. In other words, the presence of the liquid phase allows membrane-to-electrode coupling to occur extremely easily, obviating the need for sophisticated and expensive methods of bonding the catalytic particles to the membrane. In practice, assembling the cell is simply completed by juxtaposing the anode, the membrane, the GDE, and the current collector. The electric continuity within the membrane–GDE–current collector package is achieved by pressing (e.g. by applying a hydraulic pressure of 0.3–0.4 bar through the anolyte on the membrane, and through the membrane) the GDE against the rigid current collector.

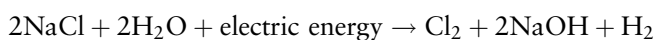
Operation of cells at higher temperatures such as 80°C , as in membrane fuel cells, is not encouraged here because of the corrosion instability of the hardware, manufactured from titanium or titanium alloy. Even without such constraints, however, this high temperature would be unwelcome as the water produced is present as steam – without the conductive bridge of the liquid phase it would be necessary to bond the catalytic particles to the membrane with all the associated problems of technology and cost.

A further advantage of the self-standing membrane and GDE is the possibility of only substituting the membrane or the GDE, whichever one is damaged.

9.3 Oxygen-depolarised cathodes for sodium chloride electrolysis

The substitution of conventional hydrogen-evolving cathodes with oxygen-consuming gas-diffusion electrodes (GDE), often referred to as oxygen-depolarised cathodes (ODC), also allows a substantial reduction in the energy consumption of the chlor-alkali process.

The global reaction of the conventional process



is replaced by the new reaction



that, in principle, should allow the same energy saving expected for the HCl electrolysis, namely about 700 kWh per tonne of Cl_2 .

The industrial realisation and development of this process, however, has been long delayed owing to the unavailability of suitable GDE. The ideal electrode, when

employed in a finite-gap cell configuration, must be able to support the reaction at practical current densities, and in the meantime act as separator between a compartment filled with gas (pure oxygen or enriched air) and a compartment filled with caustic soda (the product of the reaction).

9.3.1 Original electrode structure

The first practical example of electrodes able to satisfy many of the characteristics required in the application of chlor-alkali electrolysis is a particular family of double-sided gas-diffusion electrodes introduced some years ago under the trade name of ESNSTM, by E-TEK Inc. (now a Division of DeNora North America). The dual function (electrode and separator) of this electrode structure was achieved with an accurate choice of the basic components.

- (1) *A supporting conductive structure*, made of a nickel-wire woven net, silver-plated in order to minimise corrosion of the substrate arising from the operating conditions, and able to distribute the current uniformly all over the surface.
- (2) *An active, catalytic layer*, comprising a three-dimensional porous structure composed of a mixture of hydrophilic carbon particles (Vulcan XC-72) supporting a finely dispersed catalyst, and a hydrophobic binder (PTFE). This layer faces the liquid side and can be visualised as being formed from many hydrophobic channels (the route of the oxygen supply) and hydrophilic channels, required for the rapid removal of caustic released into the gap between the membrane and GDE.
- (3) *A pre-formed, porous, hydrophobic, electrically insulating film*, bonded by heat and pressure to the catalytic layer, used to prevent any electrolyte leakage from the liquid into the gas side that could form a film able to severely hinder the mass transport of oxygen. Liquid leakage (in the present situation that of caustic soda) is always observed and it is a clear function of the size, shape and number of cracks present in the structure, these cracks developing during sintering and cooling steps. In addition, liquid leakage is facilitated by the peculiarities of hot caustic soda, which gradually renders the PTFE domains less hydrophobic with consequent, progressive penetration into the porous structure. The degree of filling of the internal void space with caustic soda may become so high in certain extreme conditions that electrode internal flooding occurs, resulting in the decreased availability of the caustic sites and loss of performance. The porous hydrophobic film is able to prevent the liquid leakage, however, still permitting free access of oxygen gas to the catalytic layer. Nevertheless, in view of the weakness of the catalytic layer–hydrophobic film interface, especially to shear stresses, delamination occurs with the growth of large blisters that are filled with liquid, which badly affects electrode performance.

Figure 9.8 shows a typical cell voltage versus time plot for a cell fed with pure oxygen, at 85°C, operating in the current density range of 3–6 kA m⁻². The effect of delamination is clearly seen after 60–70 days on-line (DOL). Visual inspection of the GDE after disassembling the cell reveals the presence of a large blister filled with liquid that hindered oxygen access.

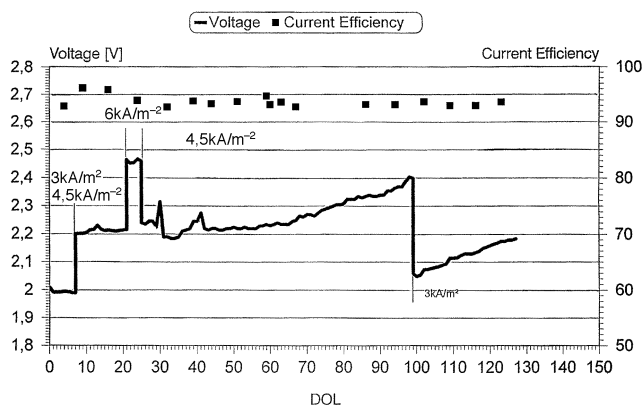


Fig. 9.8 Results of the electrolysis of NaCl using an original oxygen-depolarised cathode system.

9.3.2 Development status of the new electrode structure

The porous hydrophobic film of previous electrode designs has now been substituted with a new layer based on a mixture of particles of hydrophobic carbon and PTFE binder. This mixture is very similar in composition to the catalytic layer. This particular modification provides several advantages:

- the bonding between the gas and liquid side of the electrode is improved and in practical terms the risk of delamination is eliminated
- the use of a hot-pressing step is avoided
- the structure is less expensive
- the amount of liquid draining into the gas side is controlled and limited
- the conductive backside of the GDE allows certain design developments that were previously impossible.

This last point is particularly important. With the previous electrode type the electrical connection to the cell body could be realised along its periphery only, resulting in a poor current distribution in instances of large electrode size.

Figure 9.9 illustrates a typical plot of current density distribution across the GDE width for various types of nickel net structures. With a current supply to the back of the electrode structure there is no limitation, in principle, placed on the electrode size, at least from the point of view of current distribution. However, size limitations still

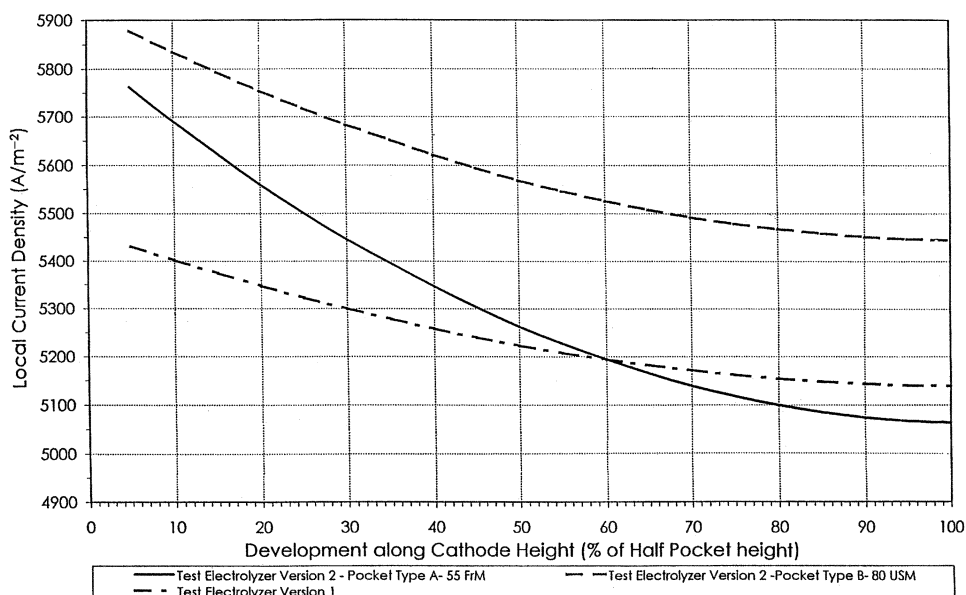


Fig. 9.9 Current density distribution along the oxygen-depolarised cathode width for various types of nickel net.

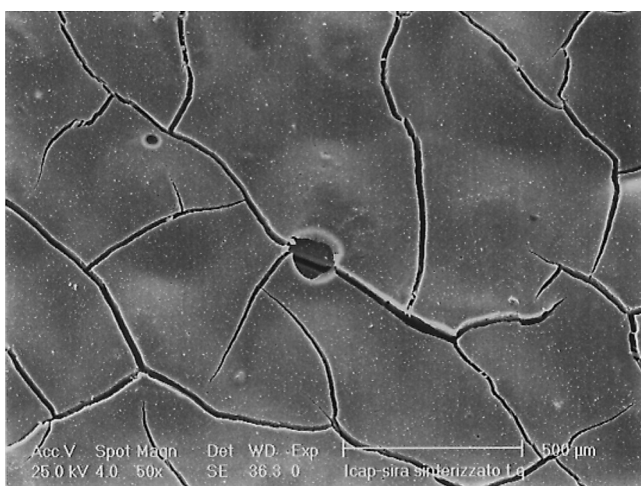
remain with the present electrode structure as a consequence of its hydraulic characteristics. Even utilising the pressure-compensation system, i.e. based on pressure-compensated gas pockets in a cascade oxygen feed type cell, the height of the electrode is not allowed to exceed a certain limit due to the pressure differential existing between the gas and the liquid side. Beyond this limit, oxygen is released into the caustic soda from the upper part of the electrode because the hydrostatic pressure, which gradually decreases with the height of the electrode, is unable to compensate for the uniform gas pressure existing on the gas side. This inconvenience can be controlled potentially in several different ways:

- by increasing the electrode thickness;
- by changing the fraction of the total volume occupied by the pores, and the ratio between average pore diameter and pore tortuosity; and
- by increasing the hydrophilic character of the liquid-side surface through the application of an additional layer that is able to retain a certain amount of electrolyte; the caustic soda penetrating into the hydrophilic layer builds up a capillary pressure inside the pores preventing large gas leaks from the structure together with the Lippmann potential under the operational voltage.

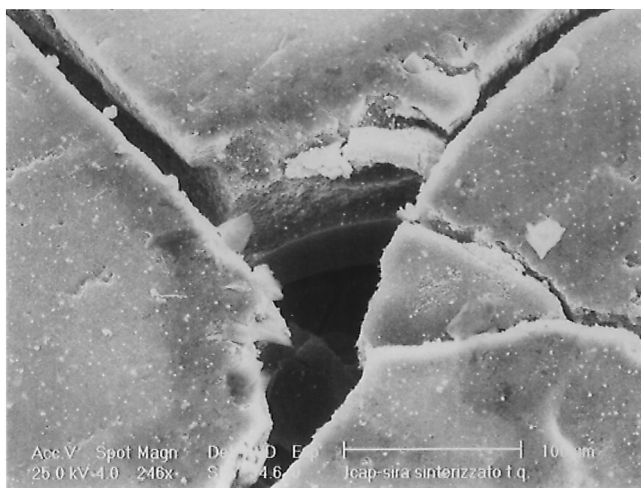
The increase of electrode thickness is an effective remedy to leaking gas, but is expensive and demonstrates some problems in the industrial production of the electrodes. The variation of the microstructure is also effective in principle, but is rather

difficult to control uniformly on a large scale. The application of the external hydrophilic layer appears to be the easiest method to control the leaking of gas and looks very attractive from the point of view of cost and production.

As mentioned previously, the gas-side hydrophobic layer does not eliminate completely the liquid drain from the gas side, a drain that may be – if only marginally – favoured by the additional liquid-side hydrophilic layer. The situation is clearly tied to the presence of cracks, which, as stated above, develop during the sintering and cooling cycles (see Fig. 9.10). The number of cracks is limited thanks to a proper temperature profile of the thermal treatment. Further, if the layer is itself comprised of a number of sub-layers, each one thermally treated before an additional sub-layer is applied, the cracks in each sub-layer do not statistically overlap, so that the popu-



(a)



(b)

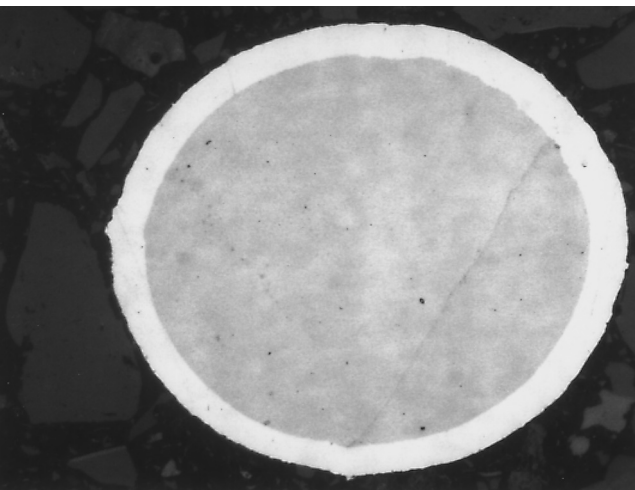
Fig. 9.10 Photomicrographs of superficial cracks existing on the gas side of the gas-diffusion electrode.

lation of cracks connecting both the gas-side and liquid-side surfaces is substantially reduced. In any case, as is discussed in a separate chapter, the liquid phase, which could penetrate into a gas pocket, is continuously drained without any measurable build-up.

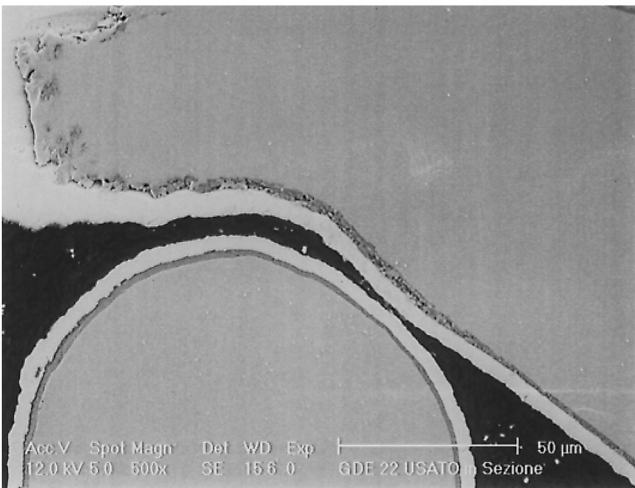
9.4 Conclusion

To complete the overview of the most recent version of the GDE, some additional information is now briefly summarised.

Electrode stability has been demonstrated (on a laboratory scale) for a period of



(a)



(b)

Fig. 9.11 A silver-plated nickel wire before and after ageing in a previous design of a GDE.

about two years. During an average period of about 100 days a gradual decrease of cell voltage is usually observed. After about one year the voltage is comparable with the voltage of the first days of operation. In principle, this behaviour can be explained in terms of increasing electrode activity and the subsequent gradual turnaround associated with deeper electrode flooding as a result of the progressive wetting caused by the permanent contact of the porous activated-carbon-PTFE mass with hot caustic soda. Another possible explanation involves the superficial oxidation of the nickel support. Analysis of GDE samples taken from previous electrolyser designs operated for long periods (more than 600 DOL) has demonstrated (see Fig. 9.11) that at the interface between the nickel support and the protective silver layer, a nickel oxide layer is formed that can contribute to the increase of the overall contact resistance. It must be noted, however, that in the presence of oxygen and at a potential of approximately -0.165 V (NHE) thermodynamics predicts the existence of nickel as nickel oxide (Fig. 9.12), which is characterised by modest electrical conductivity. From this perspective the situation is rather different from that of the traditional chlor-alkali process, where the cathode evolves hydrogen, a condition where Ni can exist as metal only.

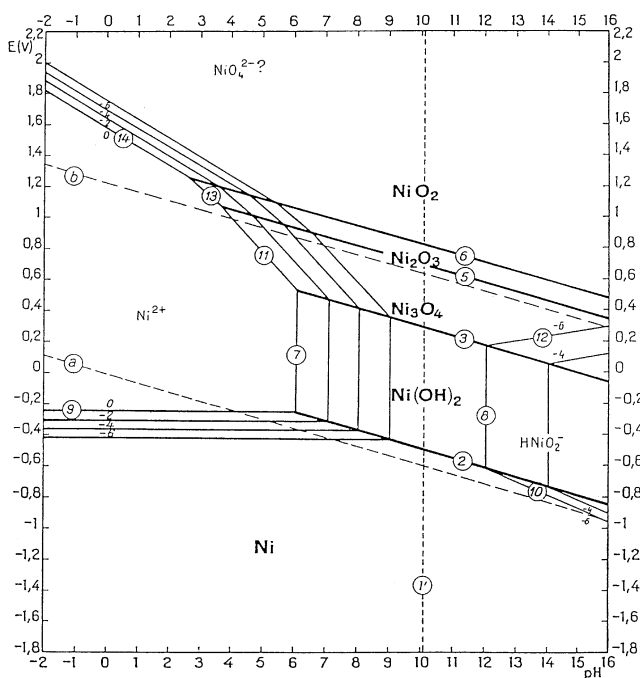


Fig. 9.12 Diagram illustrating the thermodynamic equilibria (voltage versus pH) of a nickel-water electrode system at 25°C.

Another important point to guarantee the long-term stability of the electrode is the procedure used to manage shutdowns. The experience gained through the laboratory tests shows that during shutdown the cell must be maintained under polarisation conditions to avoid the probable dissolution of the silver catalyst and its re-deposition

upon restarting operation of the cell (Fig. 9.13). This is valid mainly for an unpolarised shutdown to hot stand-by conditions.

An interesting alternative has been the development of a catalyst that is stable under all uncontrolled shutdown conditions. Figure 9.14 illustrates the very promising results of a GDE of the latest generation.

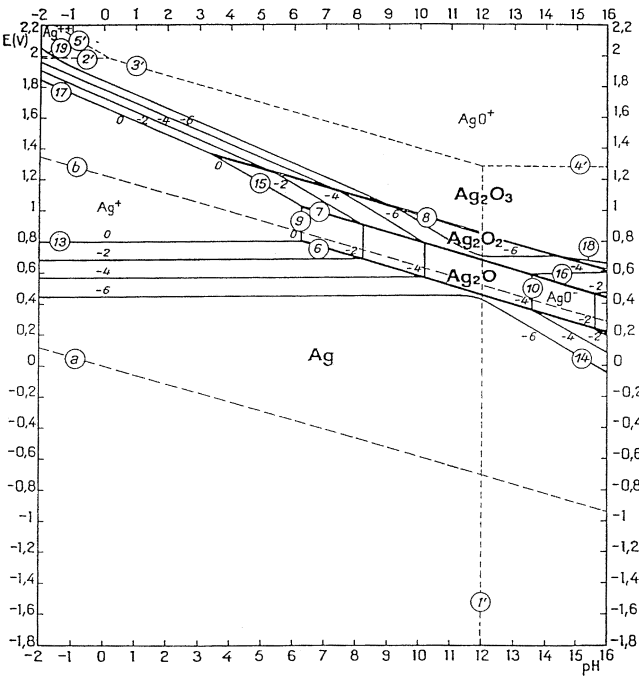


Fig. 9.13 Diagram illustrating the thermodynamic equilibria (voltage versus pH) of a silver-water electrode system at 25°C.

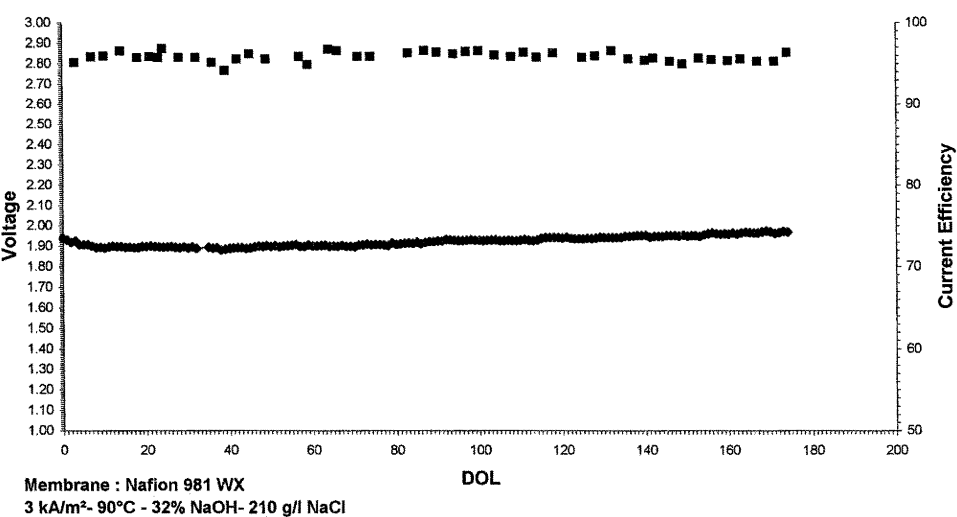


Fig. 9.14 Cell voltage results during NaCl electrolysis using a latest generation oxygen-depolarised cathode.

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3. United States Patent No. 5,598,197.

Chapter 10

Replacement of Mercury Chlor-Alkali Plants with New Membrane Plants in Australia

G R Clews

10.1 Introduction

Australia has a population of only 18 million people, spread geographically over an area similar to that of the mainland USA. The chlor-alkali industry in Australia is small by world standards and has a product mix unique in being aligned neither with chlorinated solvents nor the vinyl chain. The chlorine/caustic soda balance is heavily skewed towards caustic use in the alumina industry; however, none of the locally produced caustic soda reaches this market. This has resulted in an industry limited by outlets for the chlorine half of the ECU and based on a relatively large number of small plants scattered across the country to serve localised chlorine market needs. Australia remains a large importer of caustic soda to fill the gap between local manufacture and demand, primarily for the alumina industry.

Orica Australia Pty Ltd, formerly ICI Australia, is the largest manufacturer of chlorine and caustic soda in Australia. In December 1998, the Orica Board sanctioned a project to replace two mercury cell plants with new membrane plants. The plants are due to be commissioned sequentially at the end of 2000/mid-2001 at a total capital cost of US\$100 million.

The new plant capacities are based on a strategy of having regional plants with capacity matched to the regional market size. This has resulted in two largely identical plants being constructed to replace the existing mercury cell plants and complementing an existing membrane cell plant to provide market coverage of the eastern and southern states of Australia.

This chapter gives an overview of the chlor-alkali industry in Australia and examines the background to the decision to replace the mercury cell plants. It then describes the new plants, their technical and safety features and the process used to arrive at the selection of the technology supplier.

10.2 The chlor-alkali balance in Australia

10.2.1 Chlorine

The market for chlorine in Australia is based on the following industry segments:

- water treatment (liquid chlorine, sodium hypochlorite, ferrous chloride and ferric chloride, hydrochloric acid)
- titanium dioxide pigment manufacture (gaseous chlorine)
- steel pickling and galvanising (hydrochloric acid)
- chlorinated paraffin manufacture (plasticisers/hot-melt adhesives)
- herbicide manufacture
- pulp and paper bleaching
- general industrial use (minor chlorine use plus sodium hypochlorite and hydrochloric acid)

Local manufacture of chlorine totals 112 000 tonnes per annum.

In contrast to many other countries, chlorinated solvents and the vinyl chain are of minor importance. Carbon tetrachloride (CTC), perchloroethylene (PCE), vinyl chloride monomer (VCM) and ethylene dichloride (EDC) were manufactured for over 40 years by ICI Australia in Sydney, but the facilities were small by world standards and were progressively closed (CTC/PCE in 1991, VCM in 1996 and EDC in 1998) as they were no longer able to compete against imports from world-scale plants overseas.

Chlorinated solvents are now imported and PVC is now manufactured by Australian Vinyls Corporation in Melbourne based on imported VCM (up to 230 000 tonnes per annum of VCM or approximately 130 000 tonnes per annum of equivalent chlorine).

10.2.2 Caustic soda

The Australian market for caustic soda is some 1.4–1.5 million dry metric tonnes (DMT) per annum, of which the alumina industry utilises approximately 1.1–1.2 million DMT per annum. The next largest use is in sodium cyanide manufacture (85 000 DMT per annum).

Local manufacture of caustic is a direct function of local chlorine production and accounts for 126 000 DMT per annum, with the balance of the demand being imported. No local caustic production is used in the alumina industry. Table 10.1 summarises the caustic markets.

10.2.3 Australian chlor-alkali manufacturers

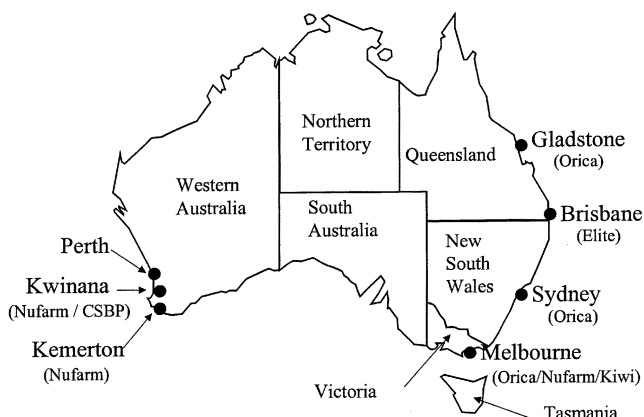
The chlor-alkali industry in Australia is dispersed, with chlorine production capacity of 127 000 tonnes per annum from a total of nine plants spread across the country.

Table 10.1 Caustic soda markets in Australia.

	Local manufacture (DMT per annum)	Imports (DMT per annum)	Total (DMT per annum)
General domestic markets	116000	34000	150000
Sodium cyanide	10000	75000	85000
Sub-total non-alumina markets	126000	109000	235000
Alumina	0	1200000	1200000
Total market	126000	1309000	1435000

The product mix reflects the market delineation described above and also the small and widely dispersed population and resource base. Output is limited by the chlorine half of the ECU and totals 112 000 tonnes per annum.

Figure 10.1 shows the location of the nine plants around Australia, while Table 10.2 shows details and capacities of these plants [1].

**Fig. 10.1** Locations of chlor-alkali plants in Australia.

10.3 Background to the project

Orica is the largest producer of chlorine in Australia and currently operates three chlor-alkali plants on the east coast. Two of these plants (in Melbourne and Sydney) are mercury cell plants dating back over 50 years while the third plant is a small, modern membrane cell plant in the central Queensland town of Gladstone. The mercury cell plants have both reached the end of their useful economic lives.

In 1996, a project was initiated to investigate options for reinvestment in the business. This was driven by a number of issues:

- (1) increasing fixed costs from operating the two mercury cell plants, particularly high maintenance costs due to large-cost end-of-life equipment failures; and
- (2) high fixed-cost of operation in terms of people numbers compared with modern plants;

Table 10.2 Chlor-alkali capacity in Australia [1].

Plant location	Capacity (tonnes per annum as chlorine)	Products	Comments
East Coast			
Orica Sydney	50000	Liquid chlorine, hypo ^a , HCl ^b , ferric chloride	Mercury cell
Melbourne	14000	Liquid chlorine, hypo, HCl, chlorinated paraffin	Mercury cell
Gladstone	9000	Liquid chlorine, hypo, HCl	ICI FM21 SP membrane cells
Nufarm (Melbourne)	6000	Gaseous chlorine to integrated herbicide manufacture	Lurgi membrane cells
Elite (Brisbane)	7000	Gaseous chlorine to hypo and HCl manufacture	Subsidiary of Ionics Inc. Ionics membrane cells
Kiwi Brands (Melbourne)	1500	Gaseous chlorine to hypo for domestic bleach	Part of Sara Lee. Ionics membrane cell
West Coast			
Nufarm Coogee (Kwinana)	17000	Gas chlorine to adjacent pigment manufacturer (Tiwest)	Lurgi membrane cells
Nufarm Coogee (Kemerton)	17000	Gaseous chlorine to adjacent pigment manufacturer (Millennium Chemicals – formerly SCM)	Lurgi membrane cells
CSBP (Kwinana)	5500	Liquid chlorine, hypo and HCl to local markets	ICI FM21 HP membrane cells
Total capacity	127000		
Total production	112000		

^a Sodium hypochlorite.^b Hydrochloric acid.

- (3) indications that mercury in caustic might become an issue in certain market segments;
- (4) progressive tightening of standards from regulators regarding mercury in effluent discharged from the plants; and
- (5) increasing pressure from regulators regarding risk contours around the mercury cell plants, which were located in increasingly urban environments.

A number of options were developed and analysed which would address these issues. The options came down to the following four:

- (1) Exit the business (close or sell).
- (2) Reinvest significant sustenance capital to bring the mercury cell plants up to the world's best practice.

- (3) Consolidate the Sydney and Melbourne plants into one new membrane cell plant in Sydney or Melbourne.
- (4) Build two new membrane cell plants – one in Sydney and one in Melbourne.

The option of building a larger plant in Melbourne to cater for the imported VCM requirement was also considered but was not financially attractive and was affected by issues relating to availability of ethylene feedstock.

The large North West Shelf project (600 000 tonnes per annum of chlorine to EDC/VCM for export), and its potential impact, was assessed if it were to go ahead. The location and the product mix are such that it was judged to have little impact on the east coast markets serviced by Orica.

McKinsey and Company were engaged to carry out a business review and to examine these options critically. The company's recommendation, based on financial and market assessments, was to move to a strategy of regional membrane cell plants in the three east-coast states, with plant capacity matched to the markets in each state.

This meant:

- expansion of the Gladstone plant to satisfy the Queensland markets
- construction of a new plant in Melbourne to satisfy the demand in Victoria, South Australia and Tasmania
- construction of a new plant in Sydney to satisfy the local New South Wales market.

Justification of the project was based purely on economics:

- savings in sustenance capital and maintenance cost required if the existing mercury cell plants were to be rehabilitated
- savings from reduced operator numbers for modern plants compared with the existing mercury cell plants
- reduced variable cost from membrane plants (lower power usage).

In addition, there were other benefits such as product quality, elimination of mercury emissions and reduced risk contours emanating from the plants.

This proposal was presented to the Board of Orica in a series of papers and finally sanctioned in December 1998, with a total cost of US\$100 million.

10.4 Plant details and location

10.4.1 Gladstone plant

The Gladstone plant is a Kvaerner Chemetics plant of 9000 tonnes per annum capacity commissioned in 1990 and using ICI FM-21 SP electrolyser. Electrolyser

capacity of only 6000 tonnes per annum was installed and the upgrade of this plant to its full design capacity was achieved in 1999 by installing an additional four electrolyzers, plus other minor modifications, at a capital cost of US\$1.4 million. This allowed the Orica Queensland market to be self-sufficient, particularly with regard to packaged liquid chlorine and hydrochloric acid.

The plant is located in a rural area some 10 km out of Gladstone and the nearest resident is many kilometres away. Pressurised chlorine storage tanks are used and the risk contours are such that there is no reason to alter this configuration.

10.4.2 Melbourne plant

The existing mercury cell plant in Melbourne (ICI Mark 1 cells) is 14 000 tonnes per annum capacity whereas the market demand in Victoria, South Australia and Tasmania is 30 000 tonnes per annum. Owing to the age, condition and location of this plant (adjacent to residential areas and 5 km from the centre of Melbourne), it was decided to close this site and construct a new Greenfield plant in Laverton North, approximately 10 km away. The new plant includes chlor-alkali manufacture, sodium hypochlorite, hydrochloric acid, liquid chlorine storage and packing and chlor-paraffin manufacture.

The plant is located in a zone set aside by the state government for heavy industry. The nearest resident is 1.5 km away and the surrounding land areas are either vacant or are filled with warehousing and general manufacturing activities. The plant occupies approximately 8 ha out of a total land area of 20 ha, with the large vacant area providing a buffer zone for risk contours from the plant. The criteria set by the state government is that the 10^{-6} individual fatality risk contour must not lie outside the site boundary and the buffer zone ensures that this is the case. The restricted location and the lack of residential areas within a 1.5 km radius ensure societal risk criteria are met.

10.4.3 Sydney plant

The Sydney plant is a combination of older mercury cell technology (updated ICI Mark 1 cells) and modern derivative plants (hydrochloric acid, sodium hypochlorite and ferric chloride) combined with liquid chlorine packing. The mercury cells had originally been in excess of 80 000 tonnes per annum capacity and cells had been progressively taken off-line following closure of chlorinated solvents (CTC/PCE) and EDC/VCM manufacture over a period of 10 years. This had left an asset significantly oversized compared with the present market demands.

The proposal for Sydney is to build a new chlor-alkali plant and feed chlorine gas to the existing derivative plants. When the present plant was built in 1944, the surrounding area was vacant. However, with the growth of Sydney, the plant is now less than 100 m from residential areas. The criterion set by the state government is that the

10^{-6} individual fatality risk contour must lie wholly outside the residential area. Societal risk criteria are also prescribed. Because of its location adjacent to large residential areas, production of liquid chlorine will cease and the new plant will manufacture chlorine gas only. Melbourne will be the central liquid chlorine manufacturing and packaging site servicing all areas other than Queensland (Gladstone produces and packs liquid chlorine for the Queensland market). This arrangement will allow the required risk criteria to be met.

An assessment was made as to whether the mercury cells only could be replaced, while re-utilising the existing brine, electrical systems etc., but this was rejected due to cost and the duration of the required shutdown period.

10.4.4 Construction of identical plants

The existing Sydney and Melbourne plants were well out of phase with market requirements in their respective states, requiring additional transport costs to move product to the market. However, the market requirements for NSW and Victoria/South Australia/Tasmania are sufficiently close that identical sized plants could be built, with significant cost savings in engineering and procurement compared with construction of two plants of differing capacity. The Melbourne and Sydney chlor-alkali plants are therefore identical up to the point of manufacture of compressed, dry chlorine. Even the plant layout has been kept identical.

10.4.5 Manning levels

Manning at a number of reference plants was extensively evaluated in order to arrive at the lowest level on the new plants. The Sydney plant will have a shift manning of three per shift and Melbourne an additional one per shift owing to the chlorinated paraffin plant (both based on a five-shift roster). Maintenance will be largely contracted out, with Orica providing personnel for planning and specialised maintenance only.

10.5 Selection of technology supplier

10.5.1 Overview

Because of the wide availability of chlor-alkali technology, it was decided to tender for fixed-price contracts for engineering, procurement and construction of the two chlor-alkali plants. The other areas – namely Outside Battery Limits for both plants and the chlor-paraffin plant in Melbourne – were managed by Orica under separate contracts. The chlor-paraffin plant process design (batch chlorination of paraffin oil and wax) was carried out in-house by Orica.

10.5.2 Chlor-alkali plant

An invitation to tender against a simple brief was sent out to a large number of chlor-alkali technology suppliers. A technical team then visited each supplier and at least one of their reference plants. Orica had a unique opportunity in that, no longer being aligned with a technology supplier (ICI Plc), it had access to all available technologies and received full co-operation from all those approached.

From these visits, a short-list of three suppliers was compiled, a very detailed specification was drawn up and a formal request to tender against this specification sent out. In addition to the standard requirements of plant capacity and product quality, the Orica specification contained the following key requirements:

- (1) It was based on minimum net operating cost over a ten-year life of operation, which considered both initial capital cost as well as ongoing costs of operation such as variable costs and maintenance costs.
- (2) Capital cost was to be minimised by use of innovative but proven process design.
- (3) A single-stream plant was required (minimum installed spares/duplicated machines) but with greater than 95% uptime.
- (4) Minimum plant manning by comparison with the reference plants.

The Orica team again visited each of the three short-listed suppliers and their reference plants.

The three tenders submitted were all of a very high standard and achieved Orica's requirements and specifications. The tender selected was therefore based on lowest net operating cost and was awarded to Kvaerner Chemetics in conjunction with Chlorine Engineers Corporation for electrolyser supply. Kvaerner Chemetics also separately contracted Kvaerner Process Australia to provide local construction management and some local design expertise.

Subsequent to awarding the contract for the two chlor-alkali plants to Kvaerner Chemetics, Orica contracted with Kvaerner Process Australia to provide services for the chlor-paraffin plant and Outside Battery Limits activities associated with the new Melbourne site, as this would bring synergies to the total project as well as potential cost savings.

10.5.3 Timing

The contracts were let in December 1998. The Melbourne plant is due to be ready for operation in December 2000 and Sydney in May 2001.

10.6 Key design features of the new plants

Each plant will utilise four Chlorine Engineers Corporation BiTAC 838 bipolar electrolyzers, with 38 cells per electrolyser operating at current densities up to

6 kA m⁻². Design capacity is 85 tonnes per day of caustic (dry) at >95% uptime. The design features are considered below.

10.6.1 Chlor-alkali process

- Use of carbon dioxide for brine treatment in place of solid sodium carbonate.
- Use of a novel Alfa-Laval plate heat exchanger system for caustic evaporation.
- Use of Kvaerner Chemetics proprietary sulphate removal technology.

10.6.2 Liquid chlorine storage

- Low-temperature atmospheric pressure chlorine storage (3 × 100 tonnes) – specified by Orica.
- High-pressure and liquid chlorine inventories (Melbourne only) specified by Orica to be contained within scrubbed buildings.
- Single-stage chlorine refrigeration system (ammonia/carbon dioxide/chlorine) with no use of ozone-depleting chemicals.

10.6.3 Chlorine packing

- Based on a benchmarked scope/specification provided by Orica and with process engineering carried out on behalf of Orica by Noram Engineers and Constructors of Canada. This package was free-issued to each supplier for detailed engineering and costing.
- Packing rates of up to 50 × 920 drums and 80 × 70 kg cylinders per eight-hour shift.
- Provision incorporated for degassing returned containers and five-yearly statutory inspection of containers.

10.7 Key safety features of the new plants

The regulatory environment is changing in Victoria with introduction from March 2000 of the Major Hazard Facilities Regulations, based on the Seveso II Directives. These are expected to flow on to the other states considered in this chapter. The key requirement of these regulations is the preparation of a Safety Case, which must demonstrate, among other requirements, that the risk from the new plant has been reduced to ‘as low as is reasonably practicable – ALARP’. The plants will incorporate a number of design features intended to reduce the risk from the facilities and demonstrate compliance with this criterion.

10.7.1 Minimising hazardous inventories

A detailed supply-chain model, which showed that two days' inventory was required to supply the forecast market demand, determined chlorine storage tank number and size. The minimum number of drums and cylinders of liquid chlorine required to be held on-site was also calculated from the supply-chain model. This approach was also extended to calculation of the number and size of storage tanks for products such as caustic soda, sodium hypochlorite and hydrochloric acid.

This provided a rational basis for storage-tank sizing and inventory levels and was also used to demonstrate compliance with the 'ALARP' principle.

10.7.2 Reducing hazardous conditions

Orica opted for a low-pressure, refrigerated chlorine storage system to reduce the hazardous conditions within the Victorian plant. The cold temperatures are maintained by withdrawing vaporising chlorine gas from the storage tanks and returning it to the compressor section. Should the refrigeration process fail, the storage tanks, having been designed as pressure vessels, can cope with hot and highly pressurised chlorine up to a temperature of 55°C.

Canned pumps are used to transfer chlorine to the packing plant and to the vaporiser for feed to the chlor-paraffin plant.

10.7.3 Minimising the duration of a release

A network of chlorine detectors is positioned at points close to potential leak sources (such as close to the chlorine vaporiser, compressor flanges and drum, cylinder and tanker filling connections) as well as along the perimeter of the site. Many chlorine detectors are interconnected with automatic plant responses and initiation of chlorine scrubbing where a chlorine release occurs within a contained building.

10.7.4 Containment of hazardous substances

Building containment

All process equipment handling and transferring liquefied chlorine (i.e. the Melbourne plant) will be located inside buildings connected to a common building scrubber. Liquefaction, bulk storage, pumping and tanker filling will take place inside the liquefaction building. This building will be closed and tanker filling interlocked with door closure. All other liquid chlorine filling (drums and cylinders) will take place in the adjacent packaging building.

Both of these buildings will normally be open and mechanically ventilated to atmosphere to provide hygienic conditions for operations. However, the doors will

automatically close on chlorine detection (with escape doors provided for personnel). In both buildings, chlorine detection will activate the building scrubber.

The design of the buildings is such that they would not be damaged in the event of 'credible events', i.e. a major chlorine release from refrigerated storage, tanker filling or package filling. They are not designed to contain the unlikely event of catastrophic rupture from a pressurised storage tank.

To enable a practical building scrubber design, bunds will be insulated to minimise the rate of evaporation from a major liquid chlorine release (i.e. at least to a rate that can be treated by the scrubber). The bunds will slope to a sump to collect small liquid spills, minimising the surface area of the spill and hence minimising the chlorine evaporation rate.

Scrubbing systems

Chlorine relieved through process venting of the plants, or released inside one of the buildings handling liquefied chlorine will be scrubbed, i.e. treated through absorption in a solution of sodium hydroxide to generate sodium hypochlorite.

Two chlorine scrubbing systems will be installed – an emergency chlorine scrubber designed to neutralise relatively small volumes of highly concentrated chlorine gas from process upsets and a building scrubber designed to neutralise large volumes of contaminated air. The emergency chlorine scrubber will operate continuously and is designed to absorb a minimum of 10 min of full chlorine production. The building scrubber will start-up on chlorine detection in the liquefaction or packaging buildings. The caustic inventory of the building scrubber is sized to treat the contents of one chlorine drum (i.e. 920 kg) over a period of 10 min, which corresponds to the worst-case release scenario in instances of a release of liquid within either of the two buildings. It is also equipped with caustic make-up/hypo withdrawal should the release exceed this size.

Both scrubbers will be supplied with three sources of electrical power – the main grid supply, a back-up grid supply from a different substation and an emergency diesel generator. In the emergency chlorine scrubber, critical equipment items will be backed-up by automatic start-up of stand-by equipment. A gravity head tank of caustic soda and a nitrogen ejector will also be provided to allow safe neutralisation of chlorine vents in the event of total power failure.

10.8 Conclusion

Orica has been presented with a unique opportunity to reinvest in an existing chlor-alkali business, to rejuvenate the business and enable it to contribute profitable returns for the next 20-plus years. This has enabled Orica to benchmark available chlor-alkali technologies currently on the market and select the one that best meets its

needs. A strategy of local plants matched to the size of their respective markets has resulted in three manufacturing sites along the east coast of Australia. The new plants meet stringent safety criteria as well as having low variable and fixed-cost structures.

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Chapter 11

Commercialisation of Kvaerner Chemetics' Sulphate Removal System

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11.1 Introduction

Kvaerner Chemetics have developed a novel, patented process [1] for the removal of multivalent anions from concentrated brine solutions. The prime market for this process is the removal of sodium sulphate from chlor-alkali and sodium chlorate brine systems. The sulphate ion in a brine solution can have a detrimental effect on ion-exchange membranes used in the production of chlorine and sodium hydroxide; consequently tight limits are imposed on the concentration of sulphate ions in brine. As brine is continuously recycled from the electrolyzers back to the saturation area, progressively more and more sulphate ions are dissolved and build up quickly in concentration to exceed the allowable process limits. A number of processes have been designed to remove sulphate ions from brine. Most of these methods are either high in capital or operating cost [2] or have large effluent flows.

The new Kvaerner Chemetics' process is low in both capital and operating costs and the effluent purge is significantly reduced. The process is based on a technique known as nanofiltration and the equipment is normally installed in a dechlorinated brine-side stream (see Fig. 11.1).

An industrial grade, skid-mounted unit (see Fig. 11.2) has been operating successfully at Occidental Chemical's Delaware City mercury cell plant since September 1997. Operating results have met both the expectations of the client and Kvaerner. This chapter discusses the operating experience at OxyChem and the resulting optimised commercial product, the Kvaerner Chemetics' Sulphate Removal System or 'SRS'. The acceptance in the market-place has been excellent; four systems have been ordered and three are in the process of manufacture, with operations commencing later in 2000. Approximately 50 firm price proposals have been issued in the past two years. Several of these evaluations are in the final stages and will lead to the sale of units in the near future.

11.2.1 Demonstration unit configuration

The design of the demonstration unit is a simple single pass of the feed brine, through six spiral-wound membrane housings, connected in series. The sulphate-rich stream is passed through the housings in series, whereas the permeate is removed from each housing in parallel. In this way the sulphate is concentrated on each pass of the reject stream and the individual permeate streams are combined to give a sulphate-lean stream.

The results from the operation show that SRS is able to operate successfully in a mercury plant, which has brine containing greater impurities than expected from brine in a membrane cell plant.

In the example shown in Fig. 11.3, a feed-stream containing a sodium sulphate concentration of 20 g l^{-1} , with a flow rate of $3.43 \text{ m}^3 \text{ h}^{-1}$, is split into two streams by the filter, namely a concentrate stream of $0.8 \text{ m}^3 \text{ h}^{-1}$, with 83 g l^{-1} of sodium sulphate and a permeate stream of $2.63 \text{ m}^3 \text{ h}^{-1}$, with a sodium sulphate concentration of 0.82 g l^{-1} . The permeate stream is returned to the brine saturators and the concentrate stream is sent to effluent.

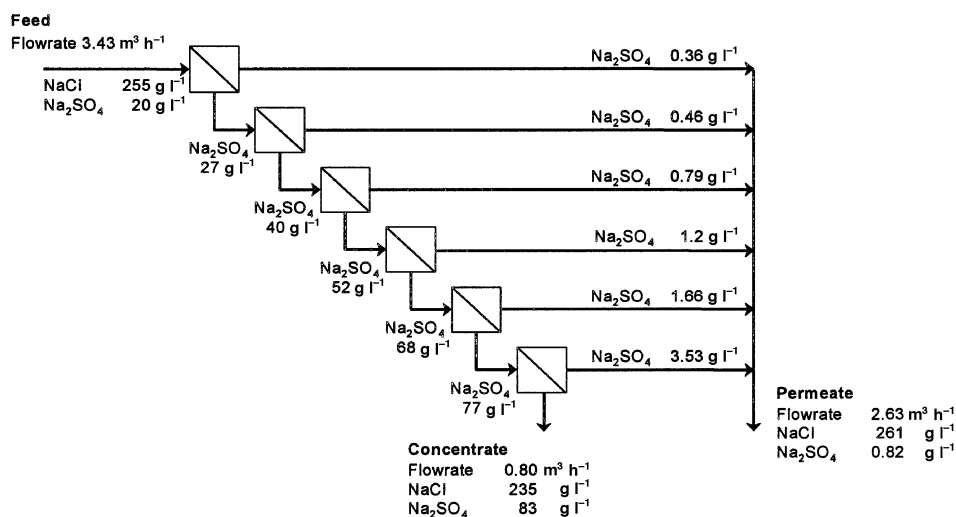


Fig. 11.3 Demonstration unit results.

11.2.2 Analysis of operating data

The trials, which were carried out in 1997 and 1998, have provided the data and understanding of the relationships between permeate flow and inlet brine velocity for different operating pressures. The graph in Fig. 11.4 shows that the brine permeability, when kept at constant inlet velocity through a standard membrane, is quite predictable for a known concentration of sulphate in the brine. The upper and lower

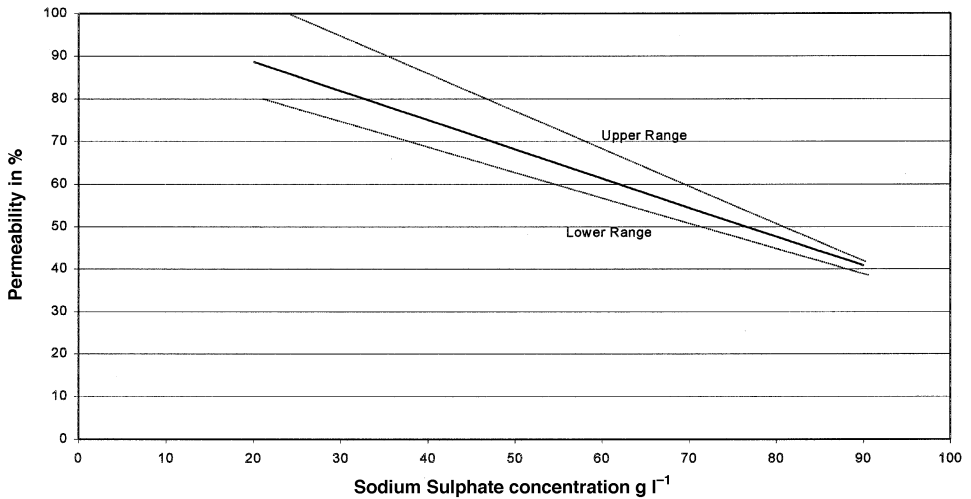


Fig. 11.4 Permeability versus sodium sulphate concentration at a fixed velocity.

range lines denote the limits of the actual data collected. In a typical membrane installation, it would be expected that the permeability through the membrane would drop by a total of 50%, from the inlet brine which contains 10 g l^{-1} sodium sulphate, to the purge brine effluent stream of 90 g l^{-1} sodium sulphate.

The operating curve for membrane permeability against inlet velocity was constructed from plant data, and curves for each sulphate concentration could be produced from normalised data. The data in Fig. 11.5 show the curve normalised to 0 g l^{-1} of sodium sulphate. This curve illustrates the relationship between the permeability and the velocity across the membrane for the existing demonstration unit.

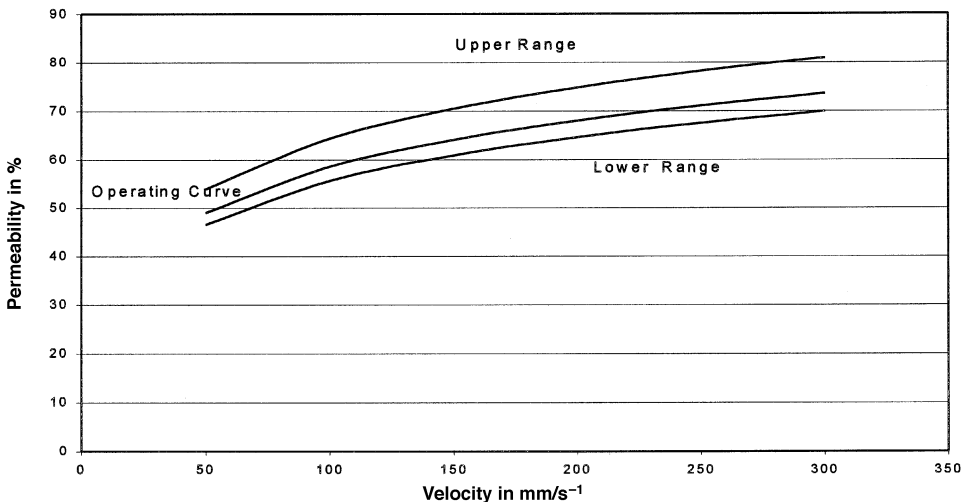


Fig. 11.5 Membrane permeability versus velocity.

11.2.3 Fouling of membranes

Membrane fouling is one of the basic obstacles to the widespread use of these types of membrane filter technologies. Indeed, during the early trials of the OxyChem demonstration unit, the permeate flow deteriorated reducing the efficiency of the unit. This was first observed as a 15% loss in recovery over a five-day period. The flow was recovered by washing the membrane in dilute hydrochloric acid. Over the next two months permeate flow reduction occurred periodically and the membranes were acid-washed to recover the flow. A systematic investigation of the unit's operation was undertaken and a membrane element was removed from the unit and returned to Kvaerner Chemetics' laboratories for analysis. The element was badly fouled – a light brown scale was observed throughout its entire length. The scale had not penetrated through the membrane but stayed on the outer surface. SEM (scanning electron microscope), EDX (energy dispersive X-ray analysis) and XRD (X-ray refraction) analyses were performed. The SEM results are shown in Figs 11.6 and 11.7. A comparison of the SEM micrographs shows that the scale is essentially removed by acid washing, returning the membrane to a cleaned state, similar to that of a new membrane.

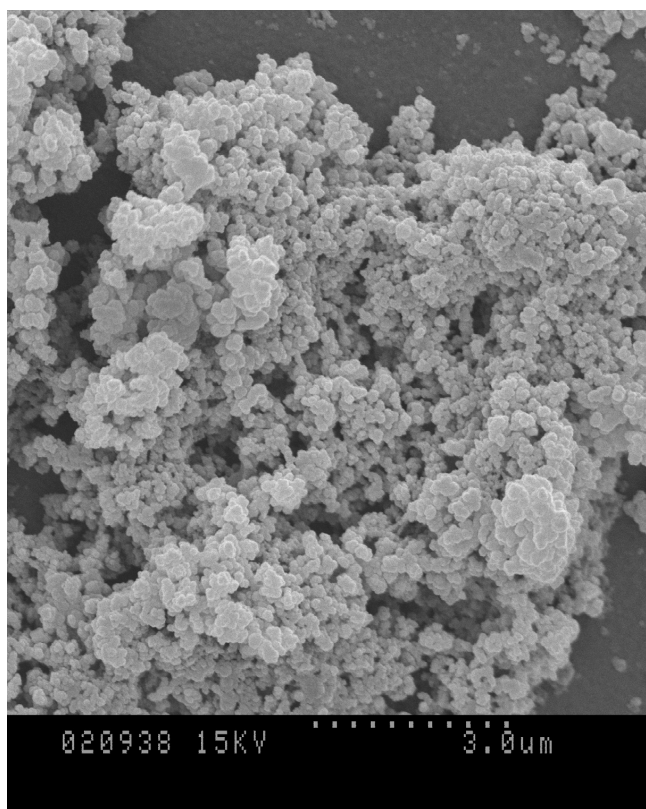


Fig. 11.6 SEM micrograph of scale deposits on the membrane.

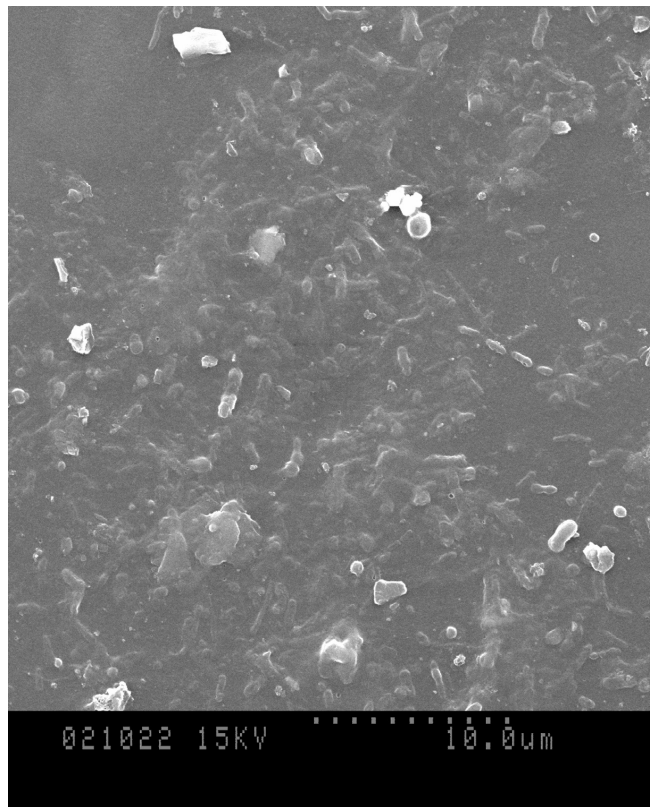


Fig. 11.7 SEM micrograph of membrane after acid cleaning.

The EDX spectrum (Fig. 11.8) shows the main surface scale impurity peaks of silica, aluminium, sodium, chloride and iron. If this EDX is compared to that of a new, clean membrane surface (Fig. 11.9), the clean surface shows sulphur, carbon and oxygen, which is typical of a porous polysulphone support. It was concluded that the scale is amorphous, composed of aluminosilicate and silicate. These compounds are normally found in trace amounts in brine solutions. Analysis showed that the surface could be cleaned with hydrochloric acid and analysis of the dissolved scale was similar to the EDX spectrum analysis. Review of the plant operation determined that the precipitation was the result of high pH in combination with high silica concentrations in the brine.

To overcome membrane scaling, the operating pH of the feed brine to the unit was lowered to a range between 4 and 7. A simple modification was made to the plant to control the pH of the plant feed brine by mixing acidic dechlorinated brine with alkaline dechlorinated brine. This modification has proven to be effective and no further membrane fouling has occurred over the last two years.

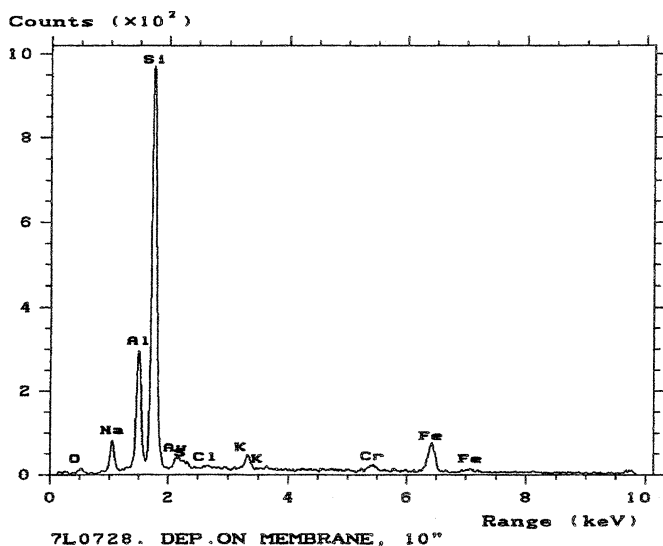


Fig. 11.8 EDX spectrum analysis of scale deposits on the membrane.

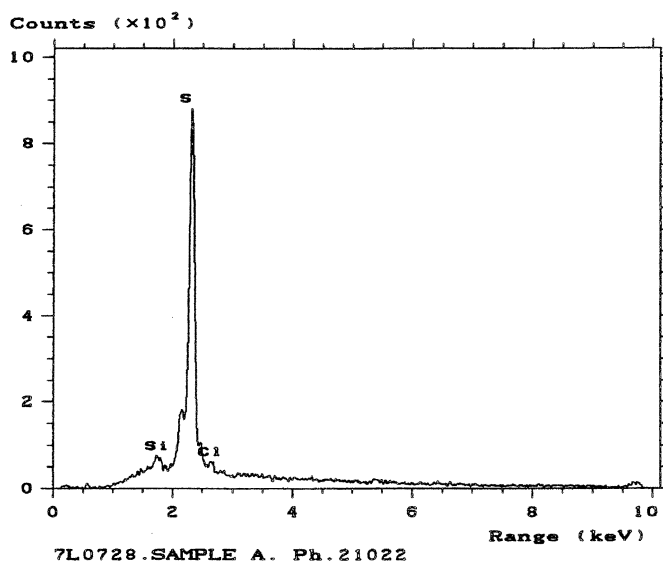


Fig. 11.9 EDX spectrum analysis of a new clean membrane.

11.2.4 Unit operation at OxyChem

The unit operation demonstrates that membrane life over two years has been demonstrated and that the selected materials of construction are correct. The recovery of sulphate-lean brine is 85–90% during normal operation. In a trial run under extreme conditions, with the unit modified to operate in recycle mode, the concentration of sodium sulphate in the reject stream was increased to 190 g l^{-1} ; a 90% sulphate rejection rate was achieved during this trial. The sodium chloride concentration decreased on the concentrate side of the membrane and increased in the

permeate to balance the feed amount. The membrane thus exhibited negative rejection of sodium chloride. Normally this unit operates with the sodium sulphate concentration kept to less than 100 g l^{-1} .

11.3 Commercialisation of SRS units

Based on our field experience at OxyChem, standard optimised SRS models have been designed to meet all required capacities. An optimum range of process conditions has been established to yield reliable, trouble-free performance. The SRS is a skid-mounted unit complete with piping and instruments to give simple and fast installation at the plant. As illustrated in Fig. 11.1, the desired quantity of sulphate is rejected as a highly concentrated sulphate stream and discharged to effluent; the return permeate stream is transferred to the saturators. The required membrane area and fluid velocities are obtained by the arrangement of a number of spiral-wound membrane elements and membrane housings. Housings are connected in parallel to provide a single stage and the stages connected in series. Figure 11.10 shows the model numbers associated with the more common three-stage units.

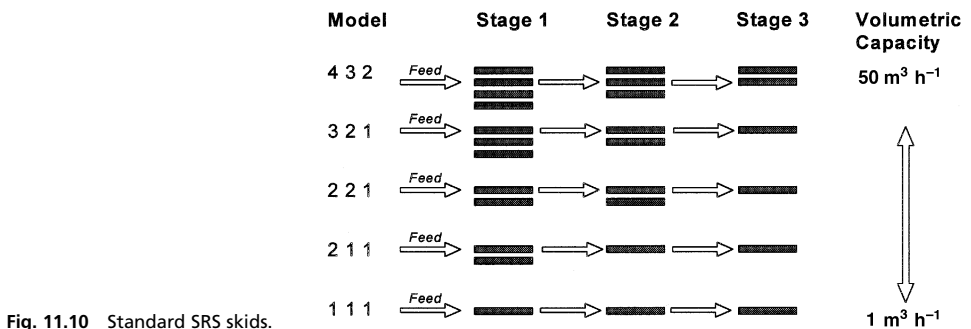


Fig. 11.10 Standard SRS skids.

For example, an SRS Model No. 221, comprises two membrane housings in the first and second stages each and one in the third stage. A range of standard SRS models is offered to meet all capacity requirements of the side-stream flow. Feed brine is fed under high pressure to the first stage. The concentrate stream, enriched in sulphate, flows in sequence to the next stage and is finally discharged at the desired sulphate concentration. A portion of the concentrated brine is recycled to increase the feed sulphate concentration. In this way the module is optimised for the client's conditions and variations in the feed conditions can easily be accommodated. The sulphate-lean permeate stream is collected in parallel from each stage and is sent back to the brine circuit. Spiral-wound membrane elements are used to maximise membrane surface area and reduce costs. The pre-designed skids reduce the overall cost and provide the client with an attractive investment payback.

11.4 Further developments

SRS skids have been proposed for a number of different types of sulphate removal operations, including sodium sulphate from sodium bromide solutions, sodium chlorate solutions and potassium sulphate from potassium chloride solutions. All of these different separations have been tested on a commercial spiral-wound membrane and the results have been good.

A single-pass experimental study used a 2.5 inch by 40 inch commercial membrane element. The recovery and reject results are calculated from:

$$\% \text{ Recovery} = (\text{volume permeate}/\text{volume feed}) \times 100$$

$$\% \text{ Rejection} = [(\text{conc. in feed} - \text{conc. in permeate})/\text{conc. in feed}] \times 100$$

The permeability of the membrane is derived from:

$$\text{Permeability} = (\text{permeate flow-rate}/\text{membrane area}) \times \text{pressure}$$

In Figs 11.4 and 11.5, permeability is shown as a percentage of a predefined permeability value.

The recovery of permeate is based on a single pass and results showing greater than 15% are considered to be good. A skid unit contains more than a single membrane (see Figs 11.3 and 11.10) and the extent of permeate recovery is cumulative through the series of membranes returning 90% of sulphate-lean brine to the circuit.

11.4.1 High temperature

The design work to produce a commercial competitive product showed that lowering the temperature of brine to less than 50°C, which was necessary in the demonstration plant, added additional equipment and installation costs to the skids. A series of experiments were carried out on a new improved membrane element, developed for higher brine temperature. In this way we could feed dechlorinated brine to the skid without addition of a cooler. The results of these experiments are shown in Table 11.1.

Rejection of sodium sulphate was exceptional at the lower temperatures but permeate recovery was low. The testing at 81°C fulfilled Kvaerner's need to reduce overall skid costs and provide good rejection with an acceptable recovery rate. The use of high temperature membranes has provided the means to optimise the number of membrane elements, reduce the equipment costs and ensure that the SRS skid is an economically attractive package.

Table 11.1 High-temperature membranes: effect of temperature on recovery and rejection.

Expt. No.	Temp. (°C)	Pressure at inlet (kPa)	Feed (g l ⁻¹)		Recovery (%)	Rejection (%)	
			NaCl	Na ₂ SO ₄		Na ₂ SO ₄	NaCl
1	25	3785	237.8	10.01	5.9	100	2.7
2	42	3800	253.8	10.12	10.1	100	3.3
3	81	3806	241.5	9.98	17.5	98.7	0.8

11.4.2 Potassium chloride

The potassium chloride and potassium sulphate system was studied. The results of tests carried out (Table 11.2) showed that the recovery levels of potassium chloride permeate were excellent at the higher operating temperatures, with almost perfect rejection of potassium sulphate. The SRS skid could be designed for use in the caustic potash industry and recover potassium chloride from effluent purges.

Table 11.2 Potassium chloride and potassium sulphate: effect of temperature on recovery and rejection.

Expt. No.	Temp. (°C)	Feed (g l ⁻¹)		Pressure at inlet (kPa)	Recovery (%)	Rejection (%)	
		KCl	K ₂ SO ₄			K ₂ SO ₄	KCl
1	73	175.37	17.23	3827	20.3	97.7	0.7
2	44	180.34	32.38	3820	0.3	93.3	2.4

11.4.3 Sodium chlorate

The SRS process is versatile in chlorate plant production. The design and operating conditions can be adapted to meet the need of the different plant requirements, e.g. production of R8 solution with reduced chromium, recovery of chlorate from the purge liquor sent to effluent, or removal of sulphate from the liquor loop.

The SRS treatment of the typical liquor of a chlorate plant has been studied. Tests have been carried out on a liquor containing 450 g l⁻¹ NaClO₃, 100 g l⁻¹ NaCl, 10 g l⁻¹ Na₂SO₄ and 5 g l⁻¹ Na₂Cr₂O₇. The results showed an average 10% recovery at 47°C, which is considered to be good (see Table 11.3).

A nanofiltration membrane will always allow the chloride and chlorate ions to pass

Table 11.3 Sodium chlorate: effect of pH on sulphate and chlorate rejection.

Expt. No.	pH	Pressure at inlet (kPa)	Rejection (%)			
			NaClO ₃	NaCl	Na ₂ SO ₄	Cr
1	8.5	3800	−0.8	0.2	99.6	93.4
2	5.74	3450	4.3	2.1	98.3	39.1
3	4.8	3450	3.0	2.5	97.4	7.9

through the membrane, whereas the sulphate is totally rejected and the proportion of rejected chromium compounds varies for the different pH levels.

11.4.4 Sodium bromide

It was expected that sulphate removal from sodium bromide solutions would be very similar to sulphate removal from sodium chloride. Experimentation was carried out to determine sulphate rejection, membrane permeability and membrane stability in concentrated sodium bromide. The experimental work determined that nanofiltration is a useful process for separating these materials.

Overall the results are similar to the data seen for sulphate rejection in sodium chloride brine (see Table 11.4). Sulphate rejection is high (>90%) and sodium bromide rejection is negligible. Permeability is greatly affected by temperature. The membrane is approximately three times as permeable at 40–45°C than at 18–20°C. However, there appears to be a slight loss in rejection at higher temperature making heating less desirable.

Table 11.4 Sodium bromide: effect of concentration and temperature on recovery and rejection.

Expt. No.	Temp. (°C)	Feed (g l ⁻¹)		Pressure at inlet (kPa)	Recovery (%)	Rejection (%)	
		NaBr	Na ₂ SO ₄			Na ₂ SO ₄	NaBr
1	25	484	9.2	3790	8.8	99.6	1.0
2	25	490	29.2	3790	8.4	97.1	–3.3
3	25	478	48.3	3790	6.5	96.4	–5.8
1	40	481	9.1	3790	21.5	95.6	1.0
2	40	490	28.8	3790	17.2	96.3	–3.7
3	40	481	47.1	3790	10.3	94.7	–5.3

The experiments determined that the membrane is not stable to bromine and like chlorine, dissolved bromine would have to be removed prior to membrane separation. However, the membrane did not lose rejection efficiency immediately, suggesting that it provides some resilience to bromine. In the event of bromine contact with the membrane, it is anticipated that the membranes will not be irreparably damaged, provided that the situation is corrected within a short time.

Table 11.5 provides the results of experiments on 80-day membrane stability that were carried out to determine whether the membrane changed after extended expo-

Table 11.5 Membrane stability: effect of long-term exposure to sodium bromide.

Expt. No.	Number of days	Temp. (°C)	Feed Na ₂ SO ₄ (g l ⁻¹)	Pressure at inlet (kPa)	Recovery (%)	Rejection Na ₂ SO ₄ (%)
1	17	25	48.3	3790	6.5	96.4
2	51	25	48.3	3780	6.5	95.6
3	80	25	47.6	3780	6.7	93.6

sure to sodium bromide brine. On each day of the 80-day period the brine was recirculated for 30 min. After 17, 51 and 80 days, runs were completed at room temperature and analysed for sulphate rejection performance. Whilst the membrane has lost some rejection over time it was stable at the end of the test period.

11.5 Summary

Having recently won the 1999 Product Achievement Award for Filter Applications from *Filtration + Separation* magazine, the SRS has become the 'state-of-the-art' technology for sulphate removal. Development of the SRS enhances Kvaerner Chemetics' record as a provider of cost-effective and environmentally friendly solutions for the chlor-alkali and sodium chlorate industries.

Capital and operating costs are low, offering a short payback in comparison to conventional methods of sulphate removal such as brine purge and barium or calcium precipitation.

For plants that use brine purge, an additional environmental benefit is the reduction of purge volumes by up to 90%. The SRS is commercially proven, having been demonstrated for over two years of successful operation in a world-scale chlor-alkali plant. The SRS has been optimised, based on field experience, to yield a fully developed and commercially competitive product.

A continuing high level of order intake and proposal activity confirms that the SRS is an attractive and viable solution for sulphate removal in modern chlor-alkali plants.

Acknowledgements

Kvaerner Chemetics acknowledges the help and support of the staff of OxyChem, Delaware City, USA for their work and contributions to make the SRS a successful project.

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Chapter 12

Process to Remove Sulphate, Iodide and Silica from Brine

T Kishi and T Matsuoka

12.1 Introduction

In ion-exchange membrane electrolysis, it is important to control impurities contained in the brine.

Chlorine Engineers Corp., Ltd introduced a new desulphation system (NDS) using zirconium hydroxide at the London International Chlorine Symposium in 1994 organised by the SCI Electrochemical Technology Group [1, 2]. As an advancement of NDS technology, Chlorine Engineers has developed a resin-type new desulphation system (RNDS®), in which ion-exchange resin containing zirconium hydroxide effectively adsorbs impurities in the brine by contact.

This chapter introduces applications of RNDS® to the removal of sulphate, iodide and silica from brine.

12.2 Removal of sulphate

12.2.1 Outline

In the brine system, sulphate ions are mixed with raw salt. These ions deposit on membranes in the electrolysis process and cause loss of current efficiency [3, 4].

Conventionally, methods such as purging, barium ion addition and freezing have been applied to control sulphate ion content in the brine feed, and as new technologies in controlling this ion, NDS and ion chromatography have been introduced [5, 6].

The RNDS® was subject to proof operation in a pilot plant for one year, after a basic examination. At present, two commercial plants are operating in Japan and in Central America.

12.2.2 Process features

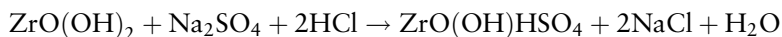
The RNDS® offers the following features:

- (1) Pollution-free. The system differs from previous chemical reaction processes. RND[®] does not use any chemicals that are harmful to the environment in compliance with ISO 14001.
- (2) Easily controlled. Membrane electrolysis processes require brine with sulphate content of no more than approximately 7.0 g l⁻¹ (as Na₂SO₄). The RND[®] achieves this level quite easily through automated control.
- (3) Low running cost. The RND[®] requires no brine purge and less chemical dosing. As the RND[®] uses dechlorinated brine at pH2, additional HCl is unnecessary, achieving minimal chemical consumption and loss of NaCl. The RND[®] consumes a small quantity of caustic soda at desorption. However, compared with former processes, the consumption is almost the same, since the amount of caustic soda needed for neutralising depleted brine is decreased.

12.2.3 Process description

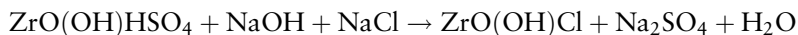
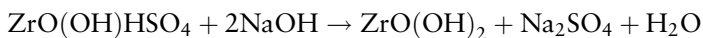
When ion-exchange resin containing zirconium hydroxide comes into contact with acidic brine in the RND[®], zirconium hydroxide adsorbs bisulphate ions; thus sulphate is removed from brine. For regeneration of the ion-exchange resin, a basic solution is supplied and when it comes into contact with the resin, sulphate desorption starts.

In the operating commercial plant, columns are filled with ion-exchange resin containing zirconium hydroxide. Acidic brine is supplied to the column from the bottom, where bisulphate ions are adsorbed, by way of a fluidised bed arrangement, based on the equations:



Upon completion of adsorption over a pre-set time, brine drains from the column. To recover the salt adhering to resin, water is supplied to the resin column from the top.

For repeated use of the resin, a regeneration process is applied. This involves supplying alkaline water to the column from the bottom, where sulphate is desorbed by way of the fluidised bed, based on the equations:



Upon completion of desorption during the pre-set time, water drains from the column. To remove sulphate adhering to the resin, water is supplied to the resin from the top of the column.

The sulphate adsorption and desorption processes run cyclically by supplying brine and water to the resin column under automatic control. A number of optional operation parameters are available.

12.2.4 Brine system and RNDS®

Figure 12.1 shows a scheme of the brine system for the membrane electrolysis process. The RNDS® is installed at the point of depleted brine flow. Figure 12.2 illustrates the principle of the RNDS® operation. The required area for the RNDS® set-up in a chlor-alkali plant having a capacity of 135 000 tonnes of NaOH per annum is 54 m².

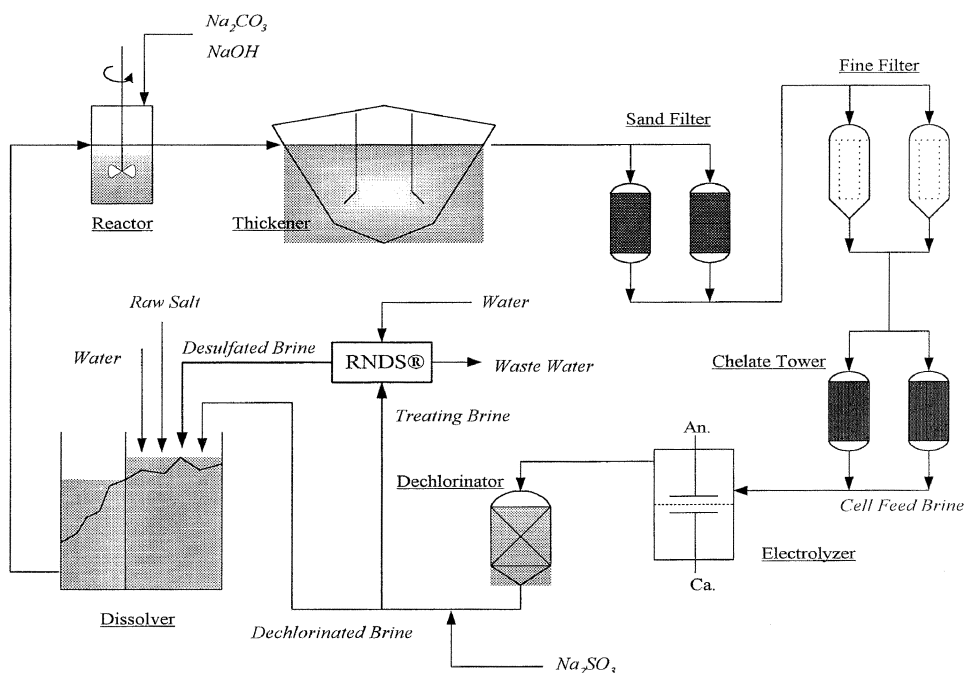


Fig. 12.1 Brine circuit of the chlor-alkali plant.

12.2.5 Example of RNDS® performance

Figure 12.3 is a plot of the sodium sulphate content in the ion-exchange resin resulting from one cycle through the RNDS® process.

12.2.6 Discussion of the desulphation process

Among the various desulphation systems available in the chlor-alkali industry, the RNDS® offers excellent advantages in terms of its low initial and running costs and environmental issues. In addition, it is a simple system and the process design results

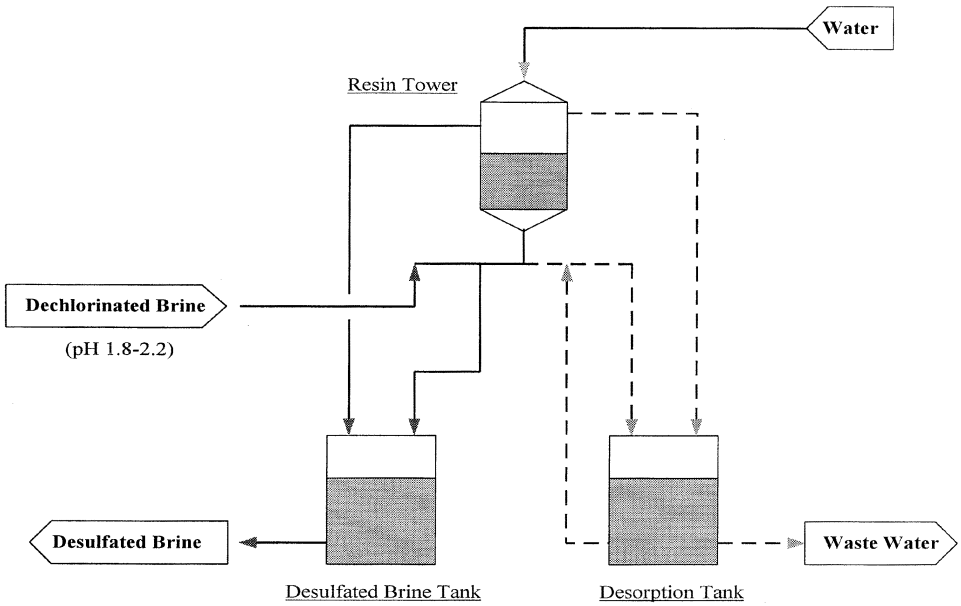


Fig. 12.2 Flow diagram of the RNDs® plant.

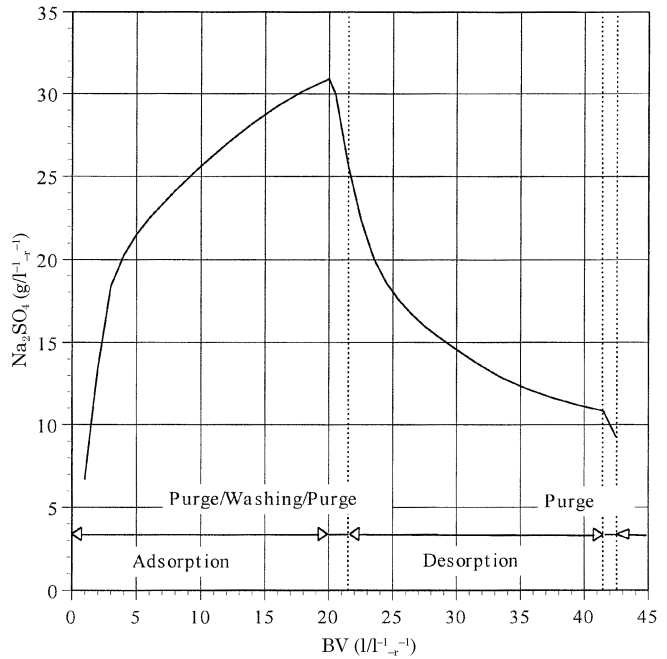


Fig. 12.3 Graph showing the quantity of sulphate adsorbed in one cycle.

Table 12.1 Overall comparison of the desulphation system.

Process	Chemical	By-product	Electrolysis ^a			Advantage	Disadvantage
			M	D	IM		
Barium	BaCl ₂ /BaCO ₃	BaSO ₄ (s)	0	0	0	Low SO ₄ level	High running cost; toxicity and solid waste affect electrode and membrane
Calcium	CaCl ₂	CaSO ₄ (s)	0	0	×	Non-toxic	High SO ₄ level
Purge			0	0	0	Easy operation	Much NaCl loss
Refrigeration		Na ₂ SO ₄ (s)	×		×	Non-toxic	High SO ₄ level
Chromatography		High SO ₄ , brine	0	0	0	Easy operation, removal of chlorate. No chemicals.	Restriction of effective chlorine concentration. Caution with heat shock. Large amount of soft water required.
Method by other ion-exchange resin		High SO ₄ , brine	0	0	0	Easy operation, removal of chlorate. No chemicals.	Restriction of effective chlorine concentration. Caution with heat shock.
NDS slurry-type adsorption	HCl and NaOH	High SO ₄ , brine	0	0	0	Low SO ₄ level. Low running cost. Non-toxic.	Requires repeated maintenance.
RNDS® fluidised bed adsorption	HCl and NaOH	High SO ₄ , brine	0	0	0	Low SO ₄ level. Low running cost. Non-toxic. Easy operation.	Restriction of effective chlorine concentration.

^a M: mercury; D: diaphragm; IM: ion-exchange membrane; 0: possible; ×: impossible.

in easy operation and reduced maintenance requirements. Tables 12.1 and 12.2 and Fig. 12.4 provide comparative data on the RNDS®.

12.3 Removal of iodide

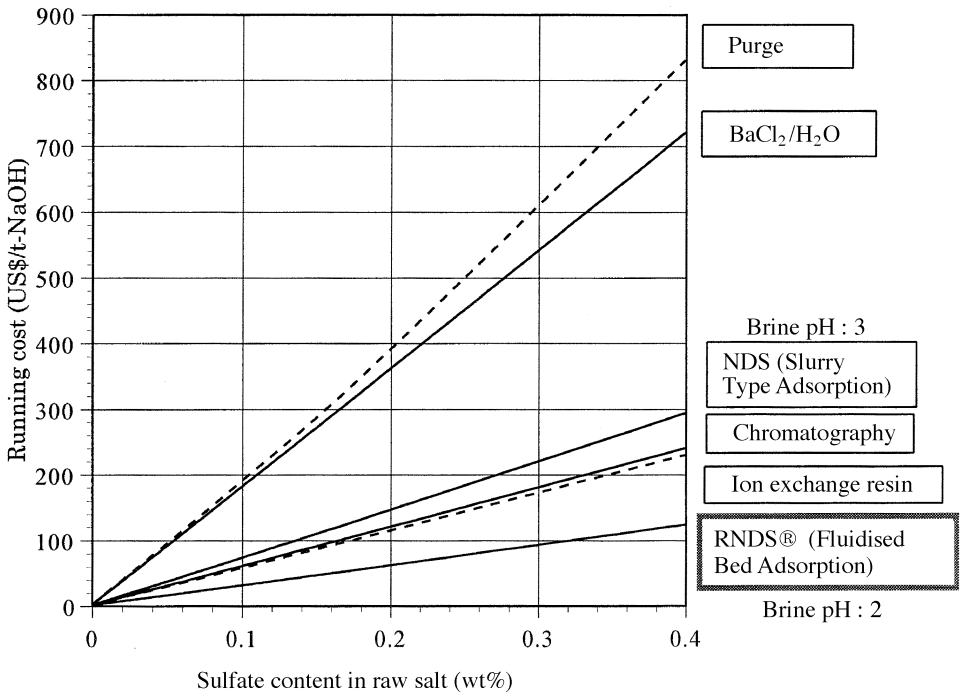
12.3.1 Outline

In the brine system, iodide is mixed with raw salt. It precipitates in membranes in the electrolysis process causing the loss of current efficiency in the membrane. Synergy effects in combination with other impurities have been reported [7, 8].

Iodide is oxidised to iodate or periodate in the membrane cell during the electrolysis process. Iodide, iodate and periodate are therefore present in the brine of a membrane electrolyser. Figure 12.5 shows comparative plots of laboratory adsorption test data for the removal of iodide and other relevant species.

Table 12.2 Typical cost comparison of the desulphation system.

Process	Ratio
Barium	—
Calcium	—
Purge	0
Refrigeration	2
NDS (slurry-type adsorption)	1.15
RNDS® (fluidised bed adsorption)	1



Remark Purge : Raw salt 33.4 US\$/ton⁻¹

BaCl₂/H₂O : including chemical and treatment cost

NDS : including chemical and adsorbent cost

RNDS® : including chemical, adsorbent, steam and power

Fig. 12.4 Running cost comparisons of desulphation systems. (Note that Purge: raw salt at US\$33.4 per ton; BaCl₂/H₂O: includes chemical and treatment costs; NDS: includes chemical and adsorbent costs; RNDS®: includes chemical, adsorbent, steam and power.)

Ion-exchange resin, containing zirconium hydroxide, is packed into the column to which brine containing iodide is supplied from the top. The observed sequence by rate of removal is: iodide ion \ll iodate ion < periodate ion.

In order to remove effectively iodide by RNDS®, oxidation of iodide to iodate or periodate is necessary. Iodide is oxidised to iodate with excess chlorine. Through contact of dechlorinated brine with the ion-exchange resin containing zirconium hydroxide, the iodide is therefore removed from the brine.

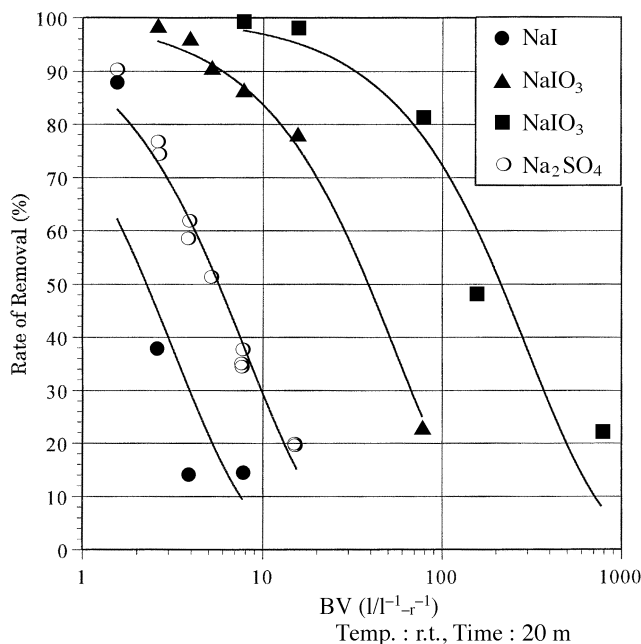
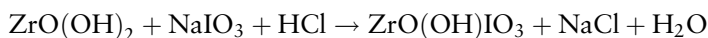


Fig. 12.5 Differing adsorption quantities by ion type.

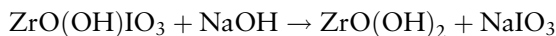
In the case of well brine, the anolyte is not circulated as the iodide content is too high. In this situation, a portion of the anolyte containing chlorine is added to the well brine and after oxidising the iodide to iodate the brine is sent to the RNDS®.

12.3.2 Process description

The column is filled with ion-exchange resin containing zirconium hydroxide. Acidic brine containing iodate ion is supplied to the column from the top. Iodate ion is adsorbed in the following reaction by way of the fixed bed:



Brine is supplied to the column until the concentration of iodate ions reaches a pre-set value, as measured at the outlet of the column. When this value has been reached, iodate ions held by the zirconium hydroxide are desorbed. Alkaline water is supplied to the column from the top. Iodate ions are desorbed in the following reaction by way of fixed bed:



Thus, by supplying brine and water cyclically to the column, iodate is adsorbed and desorbed accordingly.

12.3.3 Example of RNDS® performance

Figure 12.6 shows a scheme of the laboratory equipment used to test this set-up. Figure 12.7 is an example of the iodate concentration versus bed volume (BV) plot during one cycle of the adsorption–desorption process. Figure 12.8 shows the influence of the resin size on the extent of iodate removal. The particle size of the resin greatly influences the removal. The fluidised bed volume increases as the diameter of the resin reduces.

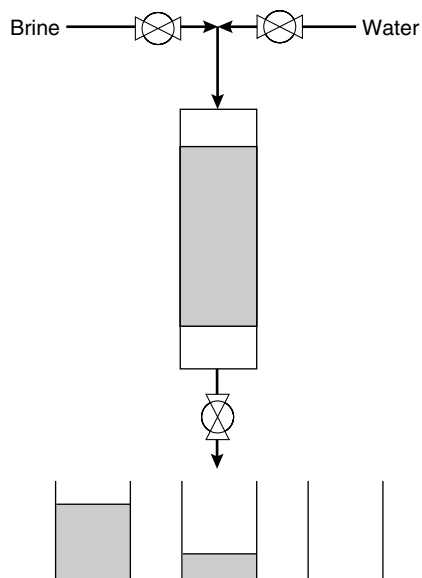


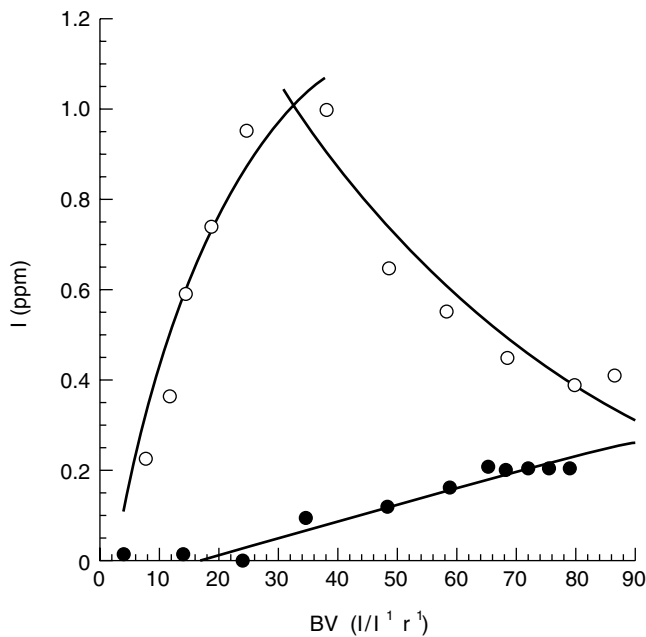
Fig. 12.6 Schematic of the examination equipment.

Figure 12.9 illustrates the influence of temperature on iodate removal. In the case of desorption at 25°C, iodate will remain on the resin particles. However, desorption is fully completed at 50°C. Figure 12.10 provides an example of an adsorption isotherm of the iodate ion.

12.4 Removal of silica

12.4.1 Outline

In the brine electrolysis system, silica is also contained in raw salt. Silica will precipitate on to membranes in the presence of calcium, strontium, aluminium and iodine resulting in the loss of current efficiency [8–10]. Silica can also be removed in a column filled with ion-exchange resin containing zirconium hydroxide, just like the iodide ion.



Adsorption

NaCl : 302.3 g l^{-1}
 I : 1.0549 ppm
 pH : 2
 Temp : R.T.

Desorption

pH : 12
 Temp. : R.T.

Fig. 12.7 Change of outflow concentrations in the adsorption and desorption processes. For adsorption: NaCl = 302.3 g l^{-1} ; I = 1.0549 ppm ; pH = 2; room temperature. For desorption: pH = 12; room temperature.

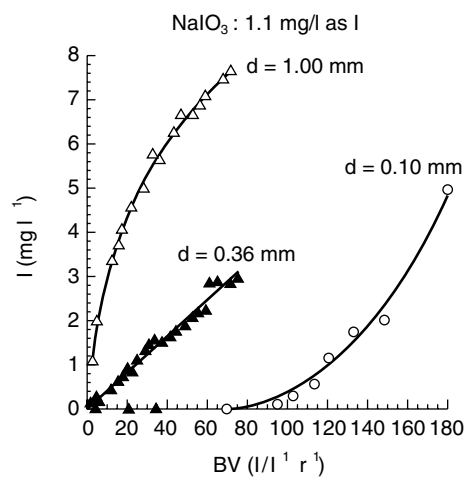
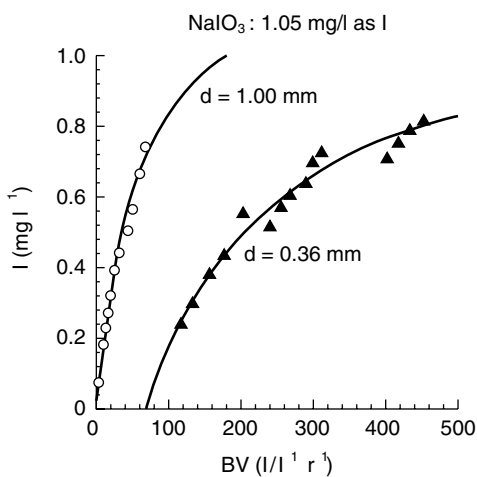


Fig. 12.8 Influence of resin size in iodate removal.

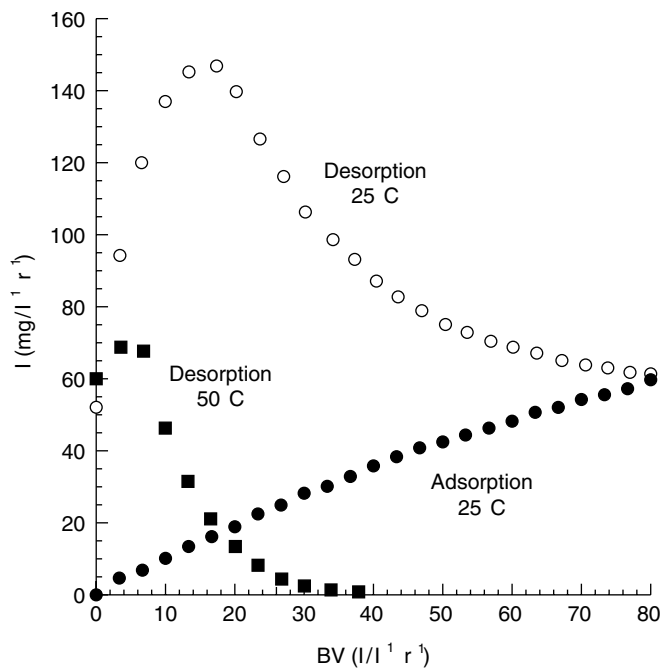


Fig. 12.9 Influence of temperature in iodate removal.

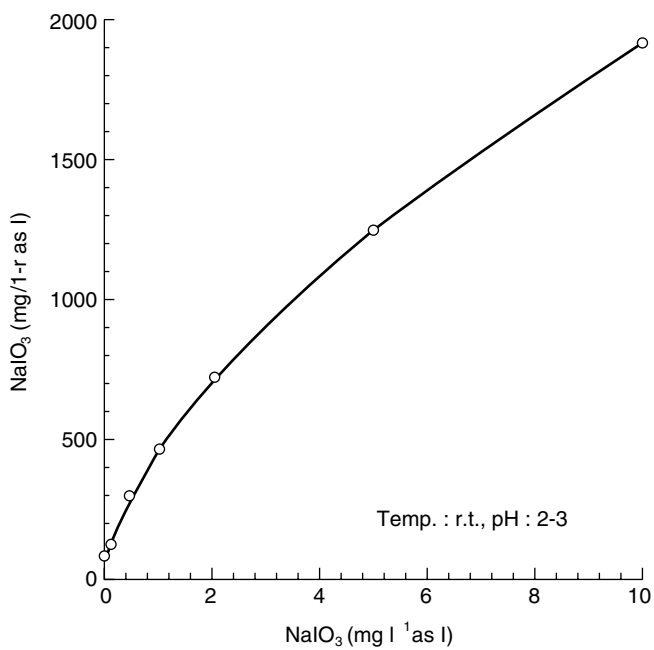
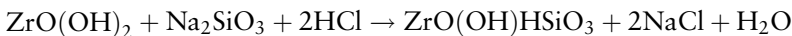


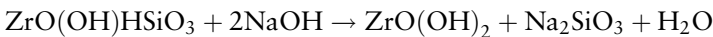
Fig. 12.10 The adsorption isotherm of iodate.

12.4.2 Process description

Acidic brine is supplied to the column and an acid metamonosilicate ion is adsorbed in the following reaction:



Alkaline water is supplied to the column and the acid metamonosilicate ion is desorbed in the following reaction:



Thus, silica can be removed easily by supplying brine and water only to the column.

12.4.3 Example of RNDs® performance

The equipment utilised in testing is that shown in Fig. 12.6 above. Figure 12.11 gives an example of the silica concentration versus bed volume (BV) plot obtained during one cycle of the adsorption–desorption process. Figure 12.12 is an example of the adsorption isotherm for silica.

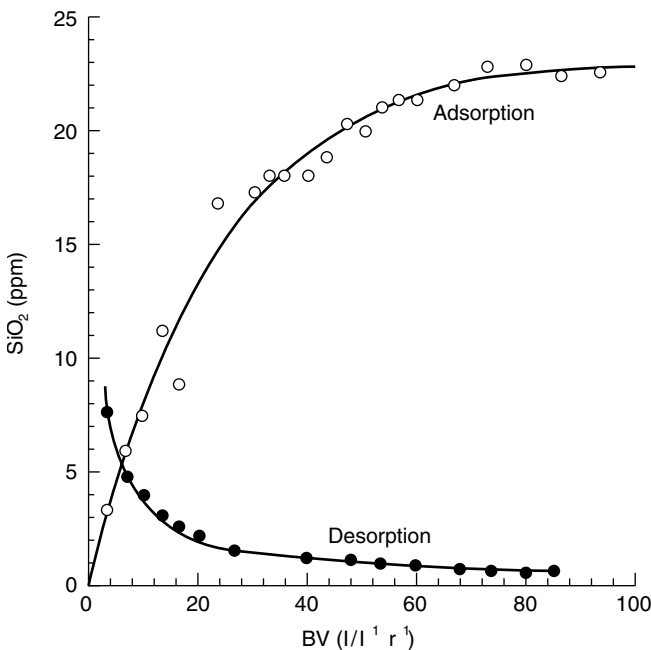


Fig. 12.11 Change of the outflow concentration from a column in the adsorption and desorption process. Both processes are at room temperature. Adsorption pH = 2.0; desorption pH = 9.0.

Adsorption	pH : 2.0	Temp. : r.t.
Desorption	pH : 9.0	Temp. : r.t.

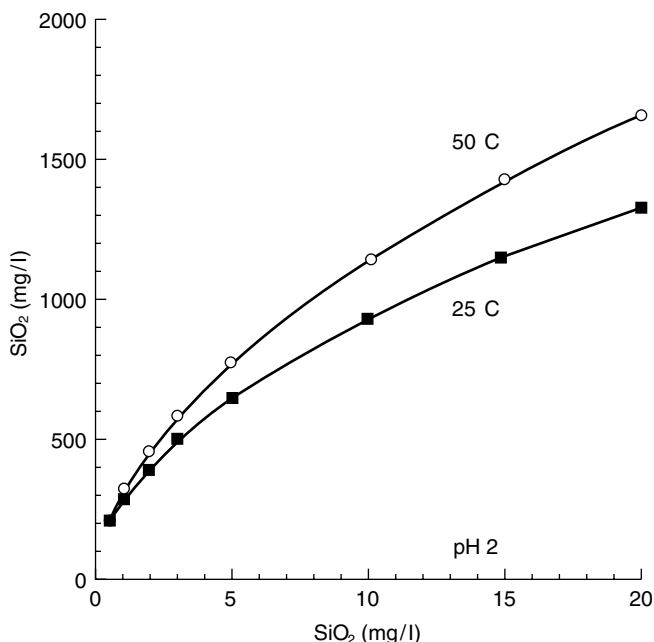


Fig. 12.12 The adsorption isotherm of silica.

12.5 Conclusion

As was mentioned previously, an effective system, RNDS[®], has been developed to remove particular impurities from brine used in membrane electrolysis procedures. The basic concept of RNDS[®] is to bring the feed brine into contact with an ion-exchange resin containing zirconium hydroxide for the adsorptive removal of impurities. For the removal of the sulphate ion from brine, commercial plants utilising RNDS[®] are already in service. For the elimination of iodide and silica, pilot-scale testing is being planned.

This chapter has introduced the RNDS[®] application in the removal of impurities from brine destined for chlor-alkali electrolysis. On top of this, however, RNDS[®] has potential use in other markets, including water treatment. Chlorine Engineers will continue its innovative work to meet the various requests coming from the chlor-alkali industry.

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Chapter 13

Advanced Diaphragm Cell Technology (ADCT)^{TM 1}

T F Florkiewicz

13.1 Introduction

At the close of the second millennium, membrane cell technology is considered the technology of choice when addressing the need for grass roots or large-scale increases in chlorine capacity. Advances over the last 20 years have been rapid and significant not only in reduced energy consumption, but also in improved cell designs leading to longer membrane life. In this same time-frame diaphragm cell technology has remained relatively constant with few major technical advancements except for developments in non-asbestos diaphragms. The recent acquisition of OxyTech Systems, Inc. by ELTECH Systems Corporation ('ELTECH') has created a marriage of diaphragm/cathode technology with anode/anode-coating technology. This marriage allows ELTECH to become more focused on providing a total package of diaphragm cell technology. The company is now realising the fruits of this marriage. Today's ELTECH team is committed not only to the improvement of each individual diaphragm cell component, but also to taking advantage of existing, and developing new, component synergies, which will positively affect total diaphragm cell performance. This integrated philosophy of both looking at the detail and analysing the whole will pave the way to refine further and continually improve diaphragm cell technology.

This integrated package by ELTECH Systems is called Advanced Diaphragm Cell Technology or ADCTTM. It has been developed for use on the MDC^{TM 2} and H-series monopolar diaphragm cells. On the anode side, various improvements in structure as well as operation result in Energy Saving Anode technology or ESA^{TM 3}. On the cathode side improvements are mainly structural and they result in the Advance Technology Cathode or ATC^{TM 4}. The ESA technology and ATC technology can be combined with ELTECH's non-asbestos Polyramix^{® 5} diaphragm, which is composed of zirconia and Teflon^{® 6}. This three-party combination forms ELTECH's Advanced Diaphragm Cell Technology or ADCT. By incorporating the use of superior gaskets, Telene^{TM 7} cell heads, and Tibac^{® 8} titanium base covers, it is possible to obtain the

full benefit of ELTECH's Long Life Diaphragm Cell technology. The entire structure is shown in Fig. 13.1.

Three years ago at this same Symposium the concept of the Long Life Diaphragm Cell was introduced. The heart of the concept is the Polyramix diaphragm, which now achieves lifetimes of five years and beyond. The long life of the Polyramix diaphragm is necessary to offset its higher cost. The focus was then to upgrade the performance of both anodes and cathodes used in conjunction with the Polyramix diaphragm to achieve additional economic benefit. Development efforts went into reducing the energy consumption of both anodes and cathodes and into optimising their performance. These development objectives were congruent with the major goal of a Long Life Diaphragm Cell. The purpose of this chapter, therefore, is to focus on the development and performance of ESA and ATC technologies, plus the further enhancement of cell operating performance using the Polyramix diaphragm.

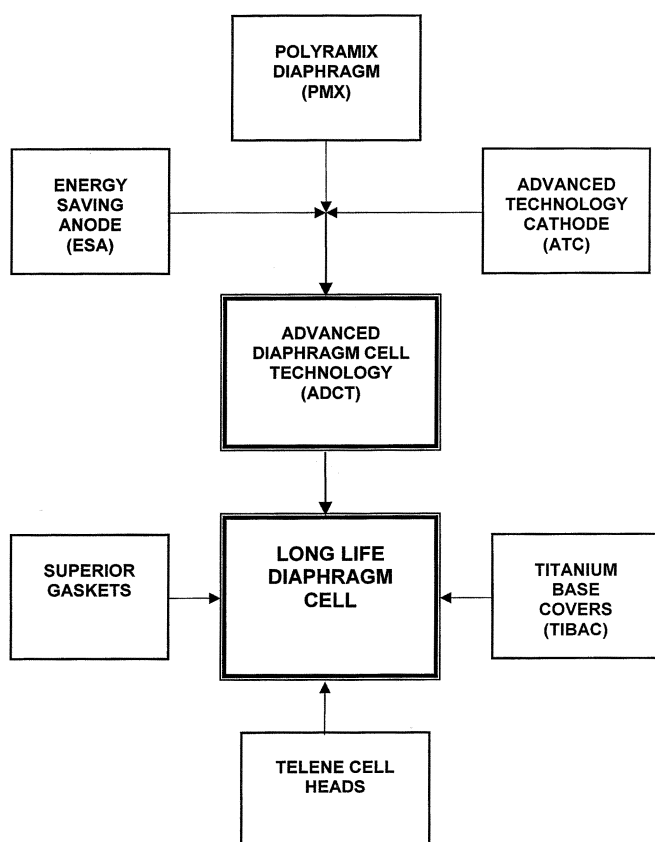


Fig. 13.1 The structure of a Long Life Diaphragm Cell.

13.2 Energy saving anodes (ESA)

The starting point for the anode design was the expandable DSA^{®9} anode. The expandable anode allowed the end-user to move the face of the anode mesh closer to the diaphragm when utilising SM-2^{TM10} polymer-modified asbestos diaphragms. To improve upon this design, a technical team was formed and the anode was broken down into its component parts – conductor bar, expanders, and mesh. The calculated voltage drops were compared with actual measurements to confirm the starting point. Structure drops of various anode designs were analysed. Manufacturing capabilities were also addressed in the study. The result was the Energy Saving Anode. The basic differences between the standard expandable anode and ESA technology are solid core conductor bars (except MDC-55 anodes), thicker re-curved expanders, and a layer of micromesh over unflattened mesh. This combination of improvements was pioneered by ELTECH through its United States Patent granted in 1975. The structural differences of the two technologies are highlighted in Table 13.1. The change in specifications has led to a reduction in anode structural voltage drop as described in Table 13.2 [1].

Table 13.1 Structural specifications of MDC-55 using ESA versus a standard expandable anode.

Component	ESA	Std. expandable anode
Conductor bar diameter (mm)	31.75	22.9
Expander thickness (mm)	1.0	0.5
Mesh size (mm)	1.5	1.5
Mesh type	Unflattened	Flattened
Micromesh size	125 mesh	n.a.
Micromesh attachment	Proprietary weld	n.a.

Table 13.2 Structural voltage-drop savings of MDC-55 ESA versus a standard expandable anode.

Component	ESA savings (mV at 2.6 kA m ⁻²)
Conductor bar	20
Expander	35
Unflattened mesh/micromesh	5
Total	60 mV

The application of the micromesh over unflattened mesh is used to reduce the current density of the anode mesh by allowing more projected surface area facing the diaphragm. The use of unflattened mesh allows the chlorine gas bubbles to escape from the surface of the anode much faster and it aids in the generation of more gas lift to further sweep the chlorine gas bubbles away from the anode surface. One further advantage is that the micromesh allows the anode to move closer to the diaphragm to provide a zero gap-type of operation. The voltage benefits of zero gap operation are covered in Section 13.4 on Advanced Diaphragm Cell Technology (ADCT). It is the

synergistic use of the Polyrax diaphragm along with the ESA technology which provides the full benefits of zero gap operation. The optimal time to consider conversion to ESA technology is when the existing anodes need re-coating or total replacement. The cost of standard re-coating can help offset the replacement of the existing anodes with ESA technology leading to an economical decision by the end-user.

13.3 Advance technology cathode (ATC)

Proceeding concurrently with the ESA design, efforts through the former OxyTech organisation were initiated to reduce the structure drop in the MDC and H-series cathodes. Again a technical team was formed and they studied the internal and external structural design of the cathode. Two critical operational effects were examined [2]. One is corrosion of the cathode internals. Active cathode surfaces are 'cathodically protected' since the cathode reaction, and hence the absorption of electrons, takes place at these surfaces. The diaphragm normally covers these surfaces. Interior cathode members, such as supports and the shell, may not be cathodically protected, particularly if they are not flooded by catholyte. Their potential can then drift from that of the active cathode surfaces. If these unprotected components are then exposed to a corrosive medium, such as hypochlorite, they are subject to corrosion. As a matter of proof the H-4 cathode was originally designed with copper rods nestled in the valleys of steel corrugations. When these internals are removed for routine replacement, the copper rods are intact but the steel corrugations are frequently corroded rather severely. Since the steel corrugations are anodic to the copper rods, they have corroded preferentially.

The second major operational effect that was studied is stress corrosion cracking. Steel is subject to corrosion caused by tensile stress when exposed to caustic soda. Stress corrosion cracking of steel usually occurs at the root of welds, but may also originate in formed or bent areas such as corners. It is more severe the higher the temperature and the higher the caustic concentration. The classic cure for such problems is to stress relieve the final assembly after all forming and welding operations have been completed. Stress relief of diaphragm cathodes has typically not been employed owing to two major factors. One is the heat distortion, which reduces the strength of the cathode mesh or perforated plate, thereby increasing the risk of deformation during diaphragm depositing. With careful selection of materials, however, structural support and fabrication technique stress relieving of the cathode mesh is possible. The second factor is that in stress relieving a completed cathode there is a risk of damaging the copper-to-steel bond, whether it is a welded, silver-brazed or explosion-bonded joint. Because of this potential risk, present work is concentrating on the effect of stress relieving explosion-bonded copper-to-steel sideplates.

With these operational effects given as a basis, it was determined that the internal

cathode tube supports or corrugations could be changed from steel to copper with no deleterious effects. This change allows a substantial reduction in structural voltage drop. In the MDC series cathode the tubesheet is also removed and the copper corrugations are welded directly to the steel sideplate as noted in Fig. 13.2.

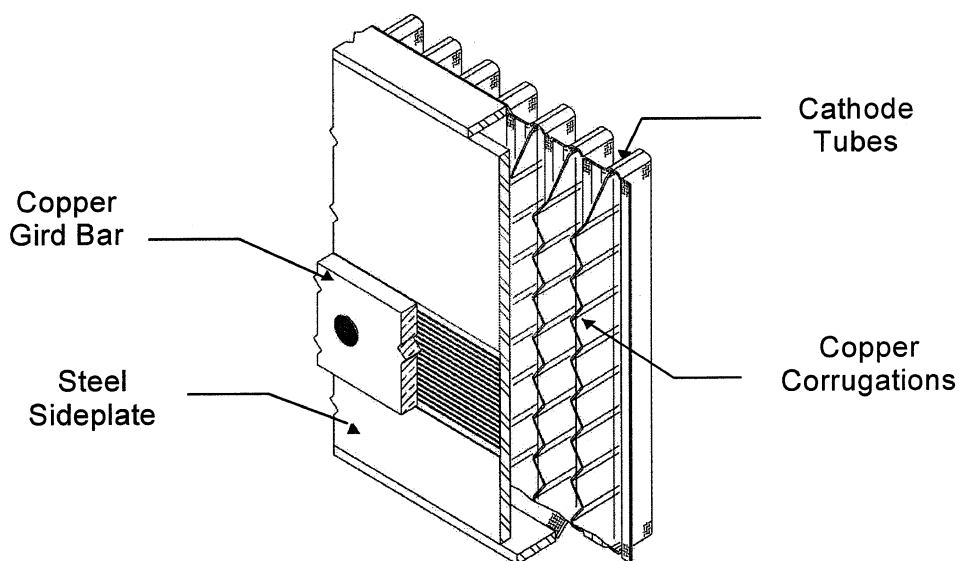


Fig. 13.2 Cross-section of an Advance Technology Cathode.

In the MDC-55 cathode the use of copper corrugations with its much higher electrical conductivity than steel, permits the removal of the copper on the 'backside' of the cathode and permits the removal of the copper 'end loops'. The backside copper plus copper 'end loops' are designed to carry about 30–40% of the current from the steel cathode tube supports, through the backside tubesheet, through the backside sideplate, and then through the end loops to the front side of the cathode. Use of copper corrugations saves the cost of the steel tubesheet, backside copper, and the copper 'end loops'. It is a substantial saving, which offsets the cost of the copper corrugations.

As with the anode, a comparison of the structural specifications of the Advance Technology Cathode (ATC) in an MDC-55 cathode is shown in Table 13.3. Voltage

Table 13.3 Structural specifications of MDC-55 using ATC versus a standard cathode.

Component	ATC	Std. cathode
Cathode tube supports	Cu corrugations	Steel channels
Tubesheet	n.a.	Steel
Backside copper	n.a.	$\frac{3}{4}$ " Cu plate
End loops	n.a.	Two, $\frac{3}{4}$ " Cu

savings are also available in the H-series cathodes to an even greater extent than the MDC series. Since each MDC and H-series cathode comes in various sizes, Table 13.4 presents the structural voltage-drop savings in each family.

Under normal operating conditions cathode internals are expected to have a useful lifetime of between 250 and 300 metric tonnes of chlorine produced per square metre of cathode area. At today's higher operating rates this equates to 8–10 years. At this time the cathode will generally exhibit thinning of the cathode tube wire mesh or perforated plate and corrosion/deterioration of steel and copper components. In the MDC series cells this means an inner assembly replacement (wire mesh cathode tubes as well as the tubesheet) and possible replacement of the front side copper sideplate. On H-series cells the process means replacement of the perforated plate cathode tubes, steel corrugations, copper rods and replacement of the front side steel sideplate. Most end-users practice a 5–10 year turnaround cycle to repair/replace the internals and either all or portions of the front side steel or copper sideplates. Thus, the most economical approach to the ATC technology is to incorporate it during the maintenance turnaround of the cathodes. In this way the cost of the regular maintenance almost offsets the cost of upgrading the cathode to ATC technology. Such a philosophy leads to extremely favourable economics with ROIs in the range of 50–70% before tax.

Table 13.4 Structural voltage-drop savings of MDC and H-series ATC versus a standard cathode.

Cathode series	ATC savings (mV at 2.60 kA m ⁻²)
MDC-55	140
MDC-29	90
H-4	186
H-2A	160

13.4 Advanced Diaphragm Cell Technology (ADCT)

Now we can combine ESA and ATC technologies with a Polyramix diaphragm and operate at zero gap to complete the Advanced Diaphragm Cell Technology package. Use of asbestos or polymer-modified asbestos cannot be used at zero gap because load swings or changes in brine flow or outages will cause the pH to vary across the diaphragm. Asbestos diaphragms will be attacked by such pH variations leading to shortened diaphragm life and lower current efficiency. The Polyramix diaphragm, being extremely stable, is able to resist the pH fluctuations. Thus, the ESA technology with the use of micromesh is ideally suited for zero gap operation using a Polyramix diaphragm. Actual operation at zero gap of a Polyramix diaphragm and ESA technology has demonstrated a voltage saving of between 100 and 200 mV depending on cell type and operating conditions.

The ADCT also leads to another dramatic improvement in diaphragm cell

operation. As with membrane cells, the ADCT package can be operated at low anolyte pH to drive the oxygen to very low concentrations (0.5–1.0% O₂) in the chlorine gas stream (on a dry and air-free basis). Low oxygen is in demand when feeding chlorine directly to an EDC reactor. The ADCT package allows the end-user to transfer diaphragm cell gas directly from the chlorine compressor to the EDC reactor saving the costly expense of chlorine liquefaction, chlorine storage, and tail-gas disposal. Figure 13.3 shows the results of over-acidification of diaphragm anolyte to reduce oxygen concentration in the cell gas.

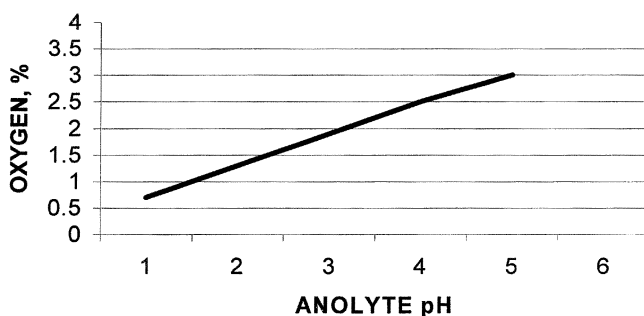


Fig. 13.3 A plot illustrating the effect of pH on oxygen concentration in the cell gas.

The ADCT package offers the following advantages:

- voltage savings attributable to ESA technology
- voltage savings attributable to ATC technology
- voltage savings attributable to zero gap operation utilising Polyramix diaphragms
- ability to over-acidify the brine feed to achieve low concentrations of oxygen in the chlorine gas stream resulting in direct chlorine gas feed to EDC reactors
- improved cathode life

Summing the power savings available for the ADCT package, which is the use of ESA, ATC, and PMX technology at zero gap, achieves 446 mV savings on an H-4-75 diaphragm cell operating at 2.6 kA m⁻². At a power cost of \$30 per thousand kWh, the operating cost benefit is \$10.90 per metric tonne of chlorine produced. This is, indeed, a substantial operating cost saving.

Of course, the ultimate goal is to combine the ADCT package with superior cell head and base gaskets, Telene cell heads, and Tibac titanium base covers to achieve the Long Life Diaphragm Cell.

13.5 Conclusions

In summary, diaphragm cell technology is not stagnant. It is alive and well and very active. Diaphragm cell technology remains a key part of ELTECH's business. It is a

business which will continue to be the major technology in the global chlor-alkali market for the next 20 years. ELTECH is committed to improving continually the technology so that the end-user can optimise the cell operation and therefore operation of the overall diaphragm plant. The advancements of ESA, ATC and PMX technologies can be used singularly or in combination to give the end-user the lowest possible operating costs particular to the specific needs of the plant. ELTECH Systems Corporation has made these major advances in diaphragm technology on entering the new millennium. The ADCT package and the Long Life Diaphragm Cell constitute another major leap forward in the pursuit of further lowering operating costs while achieving a profitable rate of return.

Notes

- ¹ ADCT is a trademark of ELTECH Systems Corporation for Advanced Diaphragm Cell Technology.
- ² MDC is a trademark of ELTECH Systems Corporation for Modified Diaphragm Cell.
- ³ ESA is a trademark of ELTECH Systems Corporation for Energy Saving Anode technology.
- ⁴ ATC is a trademark of ELTECH Systems Corporation for Advance Technology Cathode.
- ⁵ Polyramix is a registered trademark of ELTECH Systems Corporation for a polymer fibre composed of zirconia and Teflon resin.
- ⁶ Teflon is a registered trademark of E.I. DuPont de Nemours and Company for fluorocarbon resin.
- ⁷ Telene is a trademark of B.F. Goodrich for dicyclopentadiene resin.
- ⁸ Tibac is a trademark of ELTECH Systems Corporation for titanium base covers.
- ⁹ DSA is a United States registered trademark of ELTECH Systems Corporation for Dimensionally Stable Anodes.
- ¹⁰ SM-2 is a trademark of ELTECH Systems Corporation for a diaphragm modifier composed of fluorocarbon resin.

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Chapter 14

Hypochlorite Recycling to Diaphragm Cells

M Beekman

14.1 Introduction of Akzo Nobel

14.1.1 Profile

Akzo Nobel is a chemical company operating world-wide and employing over 65 000 people in more than 50 countries. The company's Head Office is located in Arnhem, The Netherlands.

14.1.2 Core activities

The range of products manufactured by Akzo Nobel includes chemicals (Chemicals Group), paints and coatings (Coatings Group) and medical care products (Pharma Group). It is Akzo Nobel's objective to gain and keep leading positions in relevant markets, and to maintain a structural profitability.

Akzo Nobel actively pursues environmental policies both where products and processes are concerned. Geographically, Akzo Nobel's activities are concentrated mainly in Europe and the United States.

14.1.3 Chemicals Group

The Chemicals Group markets over 7000 products. In addition to basic chemicals such as industrial salts, household salt, chlorine and methylamines, Akzo Nobel produces a wide range of special chemical products.

Great care and attention is given to the environmental effects both during the production and the further life-span of the product.

14.1.4 The Delfzijl site (The Netherlands)

After the discovery of a large deposit of rock salt underneath the earth's surface, and because of its logistically convenient location near the Eems estuary, it was decided to build a soda-ash plant in Delfzijl in 1954.

This plant was the beginning of what is now the Chemical Park Delfzijl. The plants on the Chemical Park now employ 1400 people, and are owned by several chemical companies. One of the plants is the Akzo Nobel Base Chemicals Diaphragm Electrolysis Plant.

14.2 The Diaphragm Electrolysis Plant

14.2.1 Plant arrangement

The Diaphragm Electrolysis Plant (Fig. 14.1) is well integrated in the Chemical Park Delfzijl. The suppliers' and customers' product-stream amounts of the Diaphragm Electrolysis Plant are optimised on the basis of the production capacity of each plant.

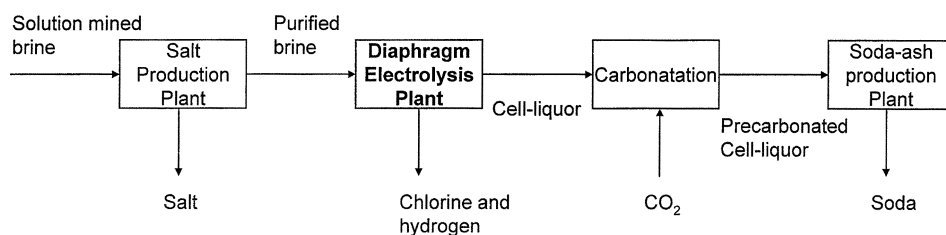


Fig. 14.1 Suppliers and cell-liquor clients of the Diaphragm Electrolysis Plant at Delfzijl, The Netherlands.

Solution-mined brine is used for salt production, and is also the feed for the diaphragm electrolysis and soda-ash production. The cell-liquor derived from the electrolysis is also used for soda-ash production after pre-carbonation.

The chlorine is used as raw material for production of chlorinated hydrocarbons by Akzo Nobel, Twaron Polymer by Acordis and CPVC by B.F. Goodrich.

14.2.2 Unit operations

The Diaphragm Electrolysis Plant Delfzijl has a cellroom containing 184 OxyTech MDC-29 cells and an annual liquefaction capacity of 130 000 tons of chlorine.

The chlorine liquefaction plant comprises a bromine-removal column, a compression-condensation unit and a Tetra absorption/distillation unit (Fig. 14.2). Waste streams of chlorine are absorbed in diluted cell-liquor in the chlorine destruction area. As a result, the destruction liquid contains sodium chloride and less sodium hydroxide than is usual. Bromine from the bromine-removal column is also added to the chlorine destruction unit. The hypochlorite solution that is formed contains a reasonable amount of bromine and salts. However, it is a hypochlorite of non-marketable quality.

Hypochlorite and hypobromite formed in the chlorine destruction unit are subse-

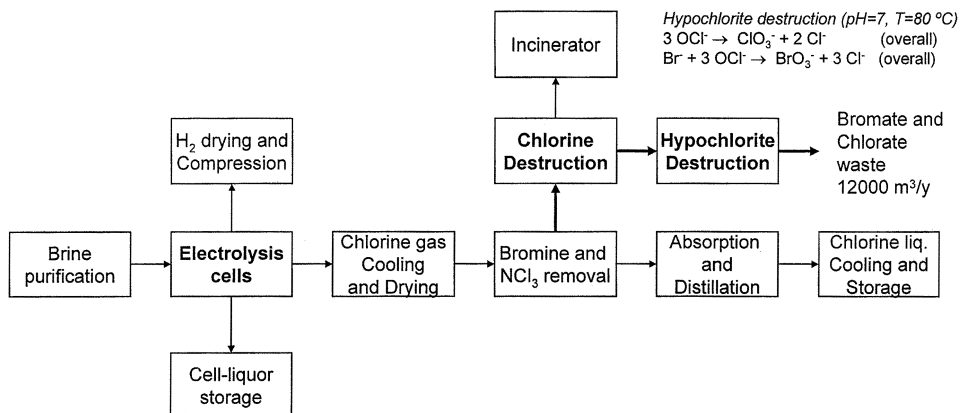


Fig. 14.2 Unit operations of the Diaphragm Electrolysis Plant at Delfzijl, The Netherlands.

quently decomposed in the hypochlorite destruction area. The hypochlorite solution was fed continuously to ideally two stirred tank reactors in series. The process conditions in this hypochlorite destruction procedure were 80°C, a neutral pH and a residence time of approximately 10 h for each reactor.

Reduced quantities of oxidative chlorate and bromate are formed, and the waste stream is allowed to feed into the Waddenzee.

14.3 Objectives of the project

Owing to a change in government regulations from 6 February 1999, regular discharges from the hypochlorite destruction unit were prohibited. Thus, it is necessary to devise an alternative method for the decomposition of the hypochlorite.

14.4 Studies

The first surveys were started in 1994, setting out to find an alternative process. Enormous amounts of work were completed by Akzo Nobel Research departments to examine the various alternatives. All results were judged on their merits.

The following processes for a solution to disposing of the hypochlorite or chlorate drains formed during the process were examined:

- (1) Catalytic destruction. Catalytic conversion of hypochlorite to chloride and oxygen can be facilitated by nickel. With the Hydecap process, ICI has a commercial solution available.
- (2) Chemical reduction. Chemical reduction of chlorate by SO_3^{2-} , SO_2 , urea or

peroxide additions is a more traditional solution. However, the variable costs are relatively high (one million Dutch guilders per year).

- (3) UV radiation. Conversion of hypochlorite to chloride and oxygen can also be realised by using ultraviolet radiation.
- (4) Biological reduction. Biological reduction of chlorate and bromate was still in development at the time of decision-making [2, 3]. It is known that this anaerobic process works well on a bench-scale. Studies on a full-scale basis are presently being conducted.
- (5) Recycle and cathodic reduction. The most elegant solution for the Diaphragm Electrolysis Plant (DEP) appears to be recycling of the hypochlorite solution and reduction of the chlorate and bromate on the cathode of the electrolysis cell – the hypochlorite solution is added to the feed brine of the cells and the chlorate and bromate are converted to chloride and bromide at the cathode.

14.5 Hypochlorite recycling and cathodic reduction

This process (see Fig. 14.3) was chosen because of the lowest variable and investment costs compared with the other options. This is a process without emissions – which is another great advantage. Bromide is discharged from the process by the cell-liquor. A small increase of bromide and chlorate concentrations in the cell-liquor is therefore expected.

There are several crucial steps in the process of recycling hypochlorite solution. First, hypochlorite is formed in the chlorine destruction where chlorine reacts with the sodium hydroxide solution. This solution is added to the brine-degassing unit. Partial conversion to chlorate and bromate takes place, which continues in the anolyte

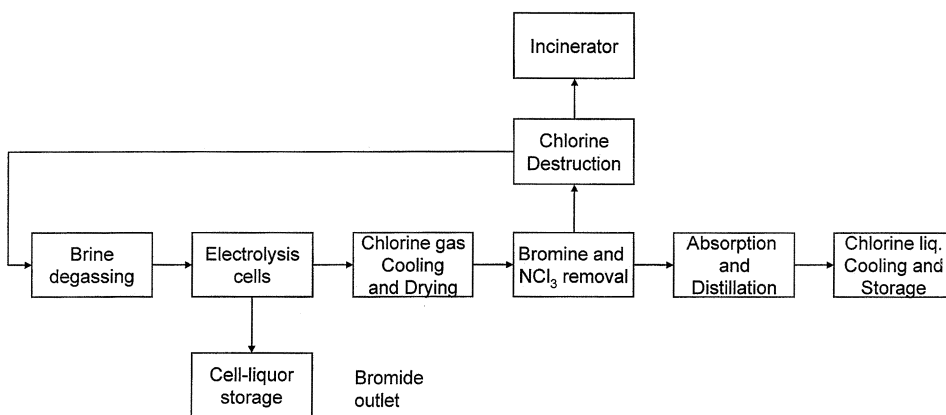


Fig. 14.3 Hypochlorite recycling and cathodic reduction.

compartment of the electrolysis cell. The anolyte flows through the diaphragm where bromate is reduced completely and chlorate partially at the cathode.

The most important chemical reactions that take place in the electrolysis process and which affect the cathodic reduction of chlorate and bromate are provided in the following subsections.

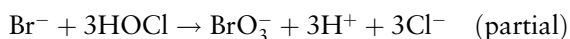
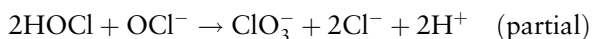
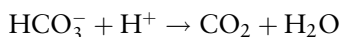
14.5.1 Chlorine destruction

The destruction of chlorine in a sodium hydroxide solution is a fast exothermic reaction. Hypochlorite, hypobromite and bromate are formed:



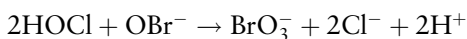
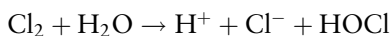
14.5.2 Brine degassing (pH = 4–5, $T = 50\text{--}80^\circ\text{C}$)

The feed brine of the DEP contains a large quantity of carbonates. Therefore, at pH5 carbon dioxide is degassed. When hypochlorite is added, chlorate and bromate are formed in the feed of the electrolysis cells. These reactions have a slow velocity. The result of this is that conversion is only partial:



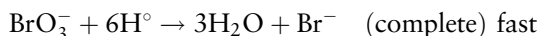
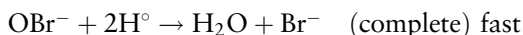
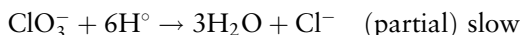
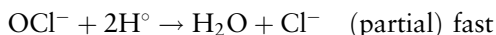
14.5.3 Anolyte compartment of the diaphragm cell

Hypochlorous acid and bromate are also formed in the electrolysis cell:



14.5.4 Cathode reaction (diaphragm cell)

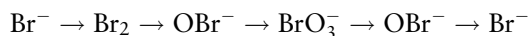
In the cell, chlorate and bromate are converted to chloride and bromide at the cathode by reduction with nascent hydrogen, although the chlorate reacts only partially. The chlorate remaining in the cell-liquor can be reduced with thiosulphate or another chemical reducing agent:



14.5.5 Bromide overall

It appears that all of the bromide that is converted to bromine and bromate in the electrolysis process is eventually recycled to the feed brine. At the cathode of the electrolysis cell bromide is formed again.

Now that the circle is closed, there is no longer any bromine-containing waste stream flowing from the destruction units. All bromide in the feed brine is returned to the cell-liquor. This is an excellent achievement for the environmental aspects of the DEP:



14.6 Results of the project

14.6.1 General

After extensive research and several tests, the option selected was recycling hypochlorite to the feed brine of the electrolysis cells. For this purpose, hypochlorite feed pipes were manufactured and the hydrochloric acid feed capacity to the brine degassing tanks was enlarged.

In addition, a vent-gas pipe leading from the degassing tanks to the chlorine destruction unit was put in place, since addition of hydrochloric acid to the brine (pH = 5) results in the evolution of carbon dioxide and some chlorine.

14.6.2 Start-up

Two days after the start-up of the installation in February 1999 it was stopped. In spite of thorough preliminary work, it appeared that the silicone hoses for the feed

brine were not resistant to chlorine-containing brine – the chlorine diffused through the silicone rubber.

Although tests had been carried out in advance, this problem was only observed in the full-scale implementation of the procedure. The scale of the laboratory tests appeared to be too small to detect this problem.

Viton hoses were instead selected for the feed brine to the electrolysis cells. These are chemically resistant to chlorine-containing brine. There are several specifications of Viton hose available. For working with brine in an electrolysis environment, special attention had to be given to rupture resistance of the hoses with respect to operator safety.

Start-up of the hypochlorite recycling process was successful in July 1999 and has been working very well since. The procedure has proved that hypochlorite recycling is indeed an excellent way to eliminate completely chlorate and bromate emissions from the hypochlorite destruction unit.

14.6.3 Results

All of the desired and foreseen objectives have been achieved.

Emissions

There are no longer any chlorate and bromate emissions from the chlorine and hypochlorite destruction units. All hypochlorite is recycled into the feed brine. This process has been operating efficiently since July 1999.

Cell-liquor

There is some increase of sodium chlorate (100 mg kg^{-1}) and sodium bromide (40 mg kg^{-1}) in the cell-liquor. This is a result of the chlorate that is formed in brine degassing. Therefore, more chlorate is fed to the electrolysis cells. Since not all the chlorate is reduced at the cathode, an increase in chlorate in the cell-liquor is observed (see Fig. 14.4).

The increase of bromide in the cell-liquor is a result of recycling all of the bromine in the plant. Almost all bromine leaves the plant via the cell-liquor as bromide. The remaining quantity of sodium bromate in the cell-liquor has not changed (8 mg kg^{-1}).

NCl_3 Production

An additional advantage of the hypochlorite recycling process is the chlorination of the feed brine in the brine-degassing unit. Organic and nitrogen-containing components are oxidised. The reaction products are removed via the vent-gas to the chlorine destruction unit. Less NCl_3 is formed in the electrolysis cells because part of the

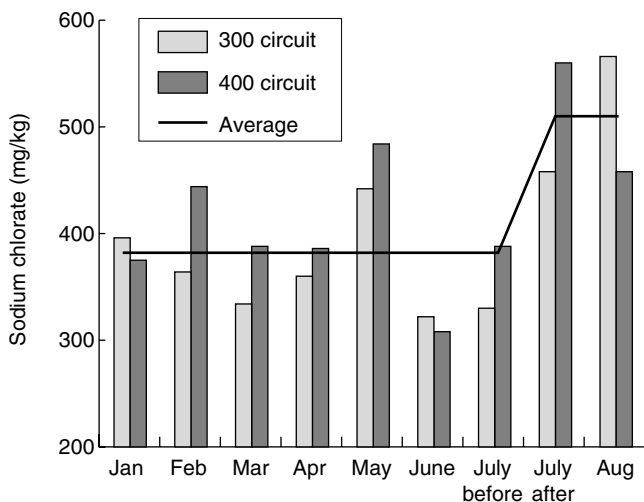


Fig. 14.4 Sodium chlorate concentration in cell-liquor before and after recycling of hypochlorite.

nitrogen is chlorinated in an earlier stage and removed (Fig. 14.5). This has advantages for controlling NCl_3 concentrations in the chlorine liquefaction. Organochlor components that are formed are removed from the brine degassing area to the vent-gas incinerator that is placed after the chlorine destruction unit of the plant.

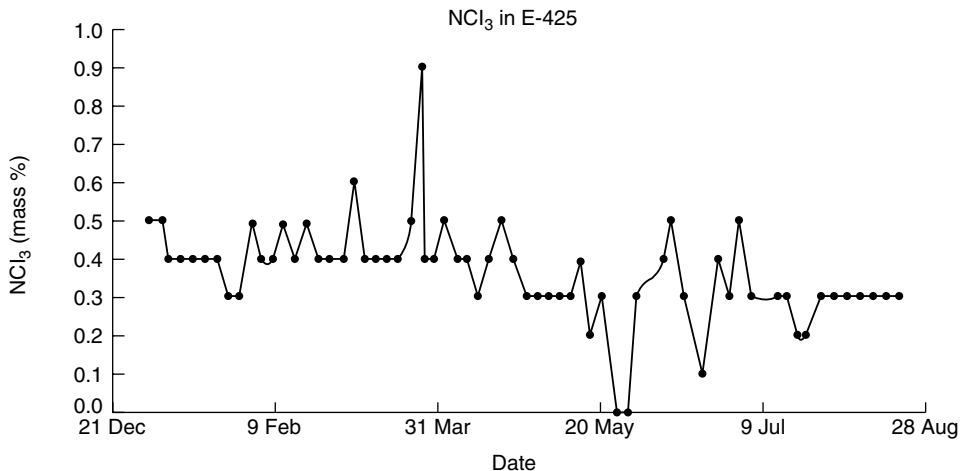


Fig. 14.5 NCl_3 concentration in the bromine removal section of the liquefaction.

14.7 Conclusions

Recycling the hypochlorite to the feed brine has provided an excellent possibility of eliminating completely the chlorate and bromate emissions of the chlorine destruction unit of a diaphragm electrolysis plant. The main advantage of the hypochlorite recycling and cathodic reduction procedure is the reduction of bromate to bromide.

An additional advantage is the oxidation of all organic and nitrogen-containing components of the brine in the brine degassing tanks. These impurities are not fed to the electrolysis cells, but the products removed to the chlorine destruction unit and incinerator. Control of NCl_3 concentrations in chlorine liquefaction has become easier.

To maintain the acidity of the brine at pH5, more hydrochloric acid is required during hypochlorite recycling to the feed brine. This extra acid demand is the cause of the largest increase of variable production costs – approximately 100 000 Dutch guilders per year. Alternative solutions showed variable costs up to one million Dutch guilders per year. The investment for this project proved to be the best economical alternative to solve the chlorate and bromate emissions problem.

The disadvantage of the hypochlorite recycling process is the small increase of chlorate and bromide concentrations in the cell-liquor. However, this is offset by higher chlorine production (0.1% more), resulting in a higher current efficiency.

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Chapter 15

Practical Operating Differences in Converting a Diaphragm Cell Chlor-Alkali Plant to a Membrane Electrolyser Plant

K Stanley

15.1 Background

Chlor-alkali manufacturers have produced caustic soda and chlorine from diaphragm cells for the whole of the twentieth century. Indeed, in some areas of the world it is the dominant technology in use today and around 20 million tonnes of caustic soda are produced each year from diaphragm cells. Much research and development are spent in refining components of the diaphragm cell to reduce power usage or prolong lifetimes. New materials for cell hoods can extend life. New ways to manufacture cathode boxes not only reduce ohmic losses but also allow re-screening to be achieved in a quicker, simpler manner. New anode structures, which reduce resistance and narrow the anode-to-diaphragm gap, provide lower operating voltages. Replacement diaphragms of synthetic materials extend the operating lifetimes and also, in the case of impregnated diaphragms, help to reduce the voltage. All of this evolving work is of benefit to the diaphragm cells of today. However, there is no escaping the fact that diaphragm cells produce a weak solution of caustic soda in brine as their by-product.

Yet more research and development effort concentrates on the diaphragm cell caustic evaporator, finding ways to aid the evaporation of the 10–12% caustic soda in brine to make it into a saleable product. Work is directed into methods of removing the salt products and impurities and preventing corrosion of the equipment. Recovery of the salt from the evaporated caustic soda is an important part of a diaphragm cell plant as the recovered salt is used in the strengthening of the feed brine.

15.2 Safety, health and environmental (SHE) aspects and the market-place

Recently, diaphragm cells have been coming under increased pressure both environmentally, by their use of asbestos in the diaphragm, and also in marketing, owing to the presence of salt in the caustic soda. SHE pressure has led to an increased awareness and use of synthetic diaphragms, of which there are several in the market.

Synthetic diaphragm suppliers claim longer lifetimes over asbestos-based diaphragms. As a result, all of the other cell components, such as gaskets and base liners, have to last at least as long. Extra brine treatment equipment is also needed in some cases to improve the feed brine quality ensuring deposits within the synthetic diaphragm are minimal. Several countries have banned, or are in the process of banning, asbestos for use in diaphragm cells. This in itself is putting pressure on producers to switch to synthetic diaphragms. Also, there are reducing supplies of suitable grades of asbestos.

Diaphragm cell caustic soda is not without its problems. Apart from the highly visible one of a price differential between it and rayon grade (mercury and membrane caustic soda) it is also being seen to cause extra corrosion in downstream process units. There is evidence of this from both the alumina and pulp industries. Also, in pulp mills, side-reactions occur, caused by the presence of salt. Pulp mills can be split into two categories: those that obtain their logs via fresh-water rivers and those that obtain their logs via the sea. That is, the logs are floated to the pulp mills through coastal waters. One log contains salt before it is brought to the pulp mill, the other does not.

Now that there is a choice of caustic soda grades as increased quantities of rayon grade become available it is evident that 'fresh water' pulp mills are seeing a difference in their process. The price differential will enable the diaphragm caustic soda to be sold, but as in any free market, market forces may wish to move to rayon grade as it becomes more widely available.

15.3 Economics

Most, if not all, of the world's diaphragm plants are written off since their average age is 15 years. This clearly has an impact on the thinking of cellroom owners when they consider the future of their assets (see Fig. 15.1).

Diaphragm cells undergo major refurbishment programmes, based around anode re-coating, since anode coating lives can typically last for 15 years or more. At this time of re-coating it is prudent to review whether to invest in new anode substrates,

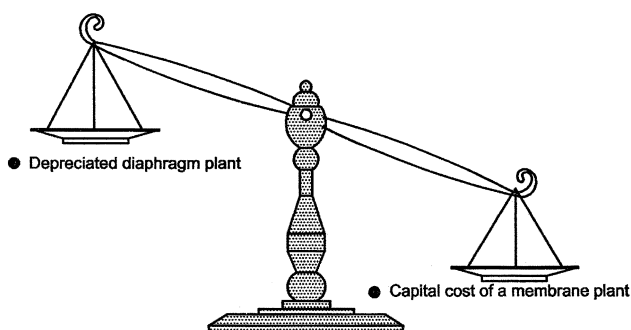


Fig. 15.1 The balance illustrating the depreciation of the old diaphragm plant versus the capital cost of a new membrane technology plant.

perhaps of a different design, to reduce power usage. Since the anodes have to be removed from their bases for re-coating this is the ideal time. Anode bases are repaired. Consideration is given to fitting titanium base covers. Cathode boxes can be repaired or re-screened completely and cell hoods may be renewed. All of this activity is a major cost in order that the diaphragm cells can continue to operate (see Fig. 15.2).

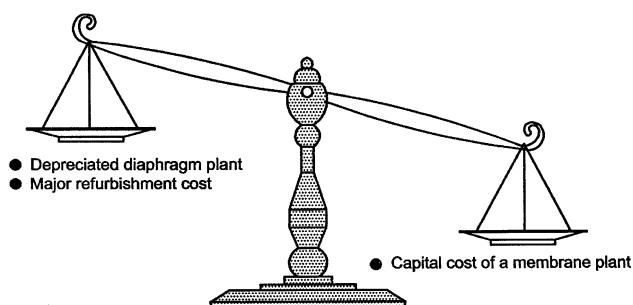


Fig. 15.2 Diaphragm plant depreciation plus refurbishment cost versus the capital cost of a new membrane technology plant.

Large though this cost is, it still does not equate to the cost of replacement membrane technology. It is estimated that the cost to refurbish all of the diaphragm cells in a 200 000 tonnes per year plant is about US\$7 million. This takes into account the items mentioned above and is based on the spend over and above the normal maintenance budget. For example, it uses the difference in cost between an asbestos diaphragm and a synthetic diaphragm, rather than the full cost of a synthetic diaphragm.

If existing diaphragm plant owners are considering conversion then the following additional benefits can also be considered. Rayon-grade caustic soda presently attracts a higher price than diaphragm grade caustic soda of around US\$15–20 per tonne. This price premium may change but even if you take a difference of US\$10 per tonne, it is still an extra US\$2 million per year income over diaphragm caustic soda for a 200 000 tonnes per year plant (see Fig. 15.3).

This premium price is now seen as independent of the cyclical market pricing of caustic soda. So how long could you expect the differential to last? The current view is that the more rayon grade, and the less diaphragm grade available, then the more the

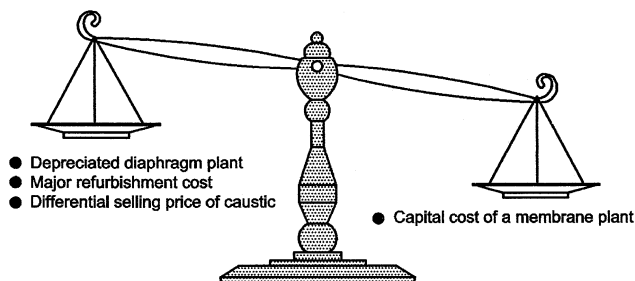
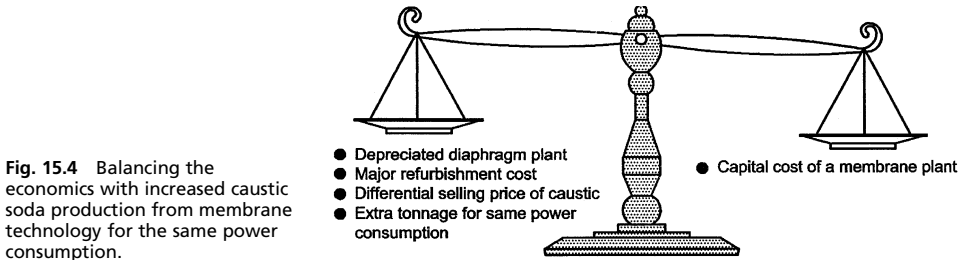


Fig. 15.3 The balance factoring the price of rayon-grade caustic soda production from membrane technology.

differential will be amplified. At that stage, of course, it is no longer a premium price for rayon grade but a discounted price for diaphragm grade caustic soda.

Another aspect that may be taken into account is that of membrane electrolyzers having a lower power consumption (Fig. 15.4). Not only does the new technology save power but it also requires less steam to evaporate the cell caustic product to 50%. Additionally, salt removal equipment required in diaphragm plants uses power. This benefit can also be turned around so that for the same power consumed by a diaphragm cell room extra volumes of rayon-grade caustic soda can be produced from the membrane electrolyzers.



As an example (Fig. 15.5) imagine a diaphragm cellroom of 200 000 tonnes per year capacity employing a rectifier producing 150 kA and 450 V. Taking the average diaphragm cell voltage as 3.6 V then the cellroom would have 124 diaphragm cells. On the other hand, membrane electrolyzers, conservatively, can have an average voltage of 3.2 V, which means that it is possible to operate an extra 16 electrolyzers for the same 450 V. These 16 electrolyzers can produce an extra 82 tonnes per day of

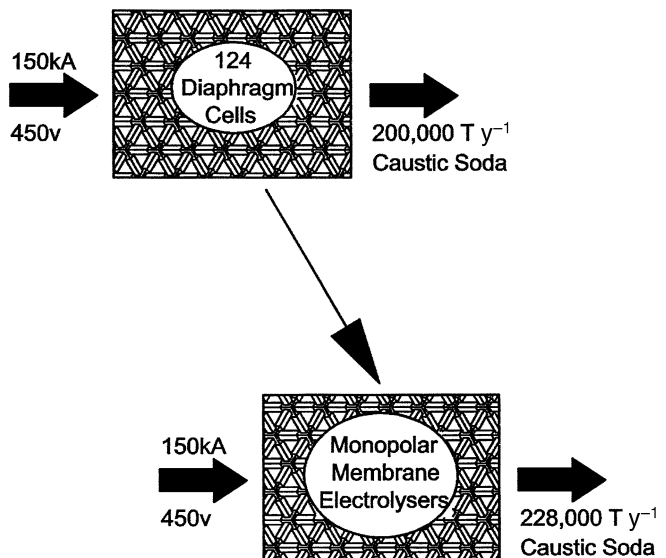


Fig. 15.5 The same tonnage of caustic soda for the same power consumption.

caustic soda, or 28 000 tonnes per year. If the price of one tonne of the combined caustic and chlorine [Electrochemical Unit (ECU) – neglecting the hydrogen] is taken as US\$250 per ECU this equates to a potential extra US\$7 million per year sales income.

Typically, a single-effect membrane caustic evaporator takes around 1.2 tonnes of steam per tonne of caustic soda while a double-effect uses around 0.7 tonne of steam per tonne of caustic soda. An equivalent single-effect diaphragm evaporator uses 4.2 tonnes per tonne. However, a well-run multiple four-effect diaphragm evaporator consumes about 2.1 tonnes of steam to produce one tonne of caustic soda. At a price of US\$20 per tonne of steam, a saving of US\$4 million per year for a 200 000 tonnes per year plant can be achieved (Fig. 15.6). So what extra equipment is required besides electrolyser?

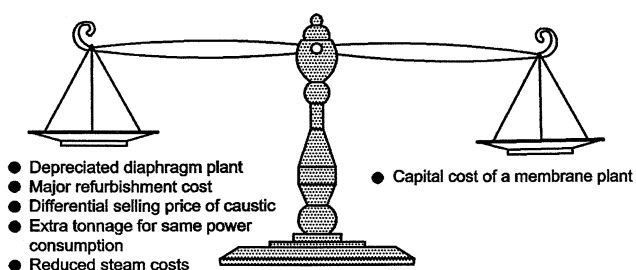


Fig. 15.6 The balance showing further savings on addition of reduced steam costs with membrane technology.

15.4 Extra equipment

The biggest single difference in converting a diaphragm plant to a membrane electrolyser is in the brine circuit. Diaphragm cells are classed as ‘once through’ since all of the brine passes through the diaphragm to end up on the cathode side as a mixture of caustic soda and brine (diaphragm cell-liquor or DCL). The strength of the caustic soda produced is dependent on cell type, diaphragm used and current density, but is typically in the range of 10–12%. On the other hand, in membrane electrolyser the membrane prohibits the passage of brine through it, so one of the products of a membrane electrolyser is a weak or depleted brine. Since this is a weak brine of around 200 g l⁻¹ it is recovered and recycled to a resaturator.

Membrane electrolyser require brine that is much purer than that used in diaphragm cells. To achieve this purity level, extra equipment is required. Diaphragm cells are usually fed brine with a hardness of around 3 ppm whereas membrane electrolyser require brine with less than 20 ppb hardness for the prolonged life of the membrane. Figure 15.7 shows the different equipment required in the brine preparation and feed section. Secondary filtration (which may be a polishing filter) may be required to remove particulate matter. The ion-exchange system reduces the hardness down to the specified level. One difference is that in a diaphragm plant, brine is strengthened in two stages – the initial stage using fresh salt strengthens the

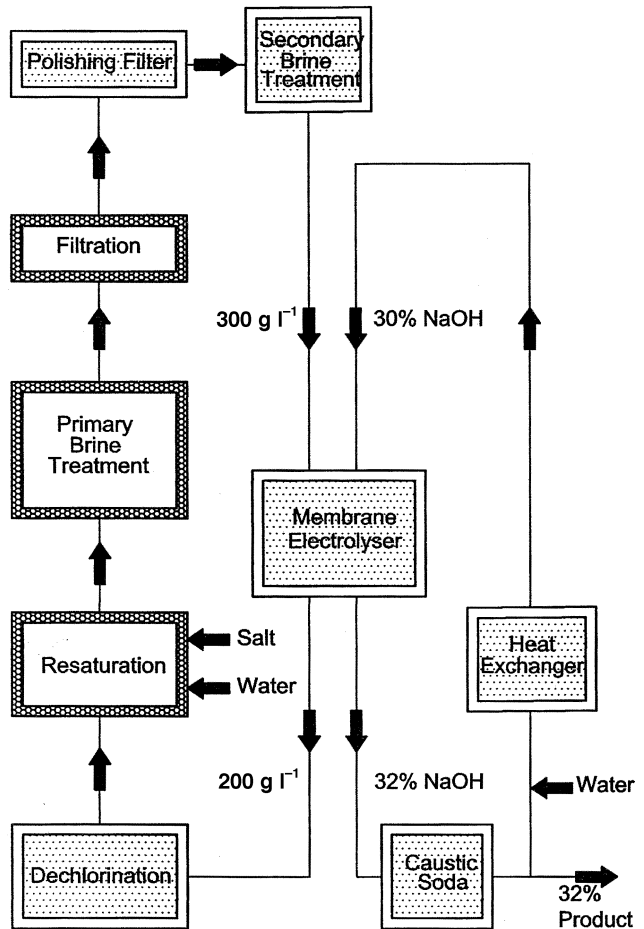


Fig. 15.7 The additional equipment required in a membrane electrolyser plant.

brine to 270 g l^{-1} whilst the second stage using recovered salt from the evaporators takes the concentration up to the required level. Since membrane electrolyser have no recovered salt from the caustic soda evaporation plant the all strengthening of the salt is achieved in the initial resaturation using fresh salt.

Variations of this method include the use of rock (mined) salt, solar salt, pure evaporated salt or the use of solution mining (brine wells) to resaturate the salt. In the latter case, weak brine can be pumped back into the brine well for reconcentration. Occasionally, this involves pipelines many miles long to transport the resaturated and weak brines. Large reservoirs are usually required at the plant to hold sufficient storage of the strong and weak brine. A means of removing the excess amount of water maybe required, either by evaporating the fresh brine to salt slurry or evaporating and concentrating the weak brine such that the water in the brine solution is balanced. What type of salt is used in the diaphragm plant will impact on what extra equipment is required for the recycled brine circuit.

The weak brine from a membrane plant contains about 0.5% dissolved chlorine. This needs to be completely removed from the brine since any chlorine in the brine will affect the ion-exchange capacity of the resin in the ion-exchange process. Initially, hydrochloric acid is added to the weak brine and the majority of the chlorine is removed in a dechlorination vessel. These dechlorinators can either be air-purged or under vacuum. The chlorine removed is either fed back into the plant as a strong chlorine or fed to a sodium hypochlorite plant as a weak chlorine in air to be made into bleach. These systems usually reduce the chlorine content of the brine to around 20 ppm. This is still too high and secondary dechlorination is required by either adding chemicals, such as hydrogen peroxide or sodium thiosulphate, or use of an activated carbon bed.

The chlorine-free brine, still as a weak solution, can then be recirculated to the resaturator. Care should be taken in partial or staged conversions not to feed any diaphragm cell evaporated salt to membrane electrolyzers as it may contain chromium and nickel from the evaporators, which are harmful to the membrane.

15.5 Space requirements

Taking a 200 000 tonnes per year plant as an example, the foot-print for a diaphragm technology plant is shown in Fig. 15.8. A diaphragm plant would typically consist of around 124 cells laid out in four rows with the electrical circuit as a W shape. Owing to the length of the rows, access points are allowed midway down the rows for safety. Taking as an average that the installed diaphragm cell centres are 2.35 m, a cellroom of 75 m by 26 m or 1950 m² is required.

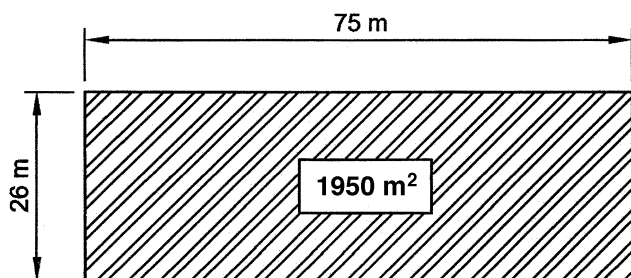


Fig. 15.8 Area required for a typical diaphragm plant.

For the membrane cellroom of the same capacity there are two choices of technology type: either monopolar or bipolar electrolyzers. In the case of monopolar membrane electrolyzers (Fig. 15.9), such as the ICI FM1500, one membrane electrolyser can replace one diaphragm cell. Since the membrane electrolyser has smaller dimensions there is an overall space saving. The monopolar membrane electrolyzers may use the same pipework galleries and overhead crane from the

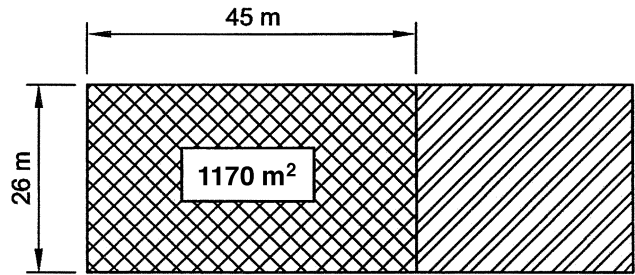


Fig. 15.9 Area required for a membrane (monopolar) plant.

diaphragm cellroom. For the same production a cellroom of 45 m by 26 m or 1170 m² is required.

If bipolar membrane electrolyzers are installed (Fig. 15.10), such as the ICI BiChlor, then even less floor area is required for the same production capacity. In both membrane cases the space available also depends on the chosen operating current density. Utilising the 150 kA available, nine bipolar electrolyzers can operate up to 16.7 kA each. This would require 112 anodes per electrolyser to manufacture the 200 000 tonnes per year of caustic soda, utilising about 360 V of the 450 V available. With bipolar electrolyser centres of 6.5 m, including operator walkways, an area of around 60 m by 14 m or 840 m² will be required. However, more extensive pipework modifications are required with bipolar arrangements.

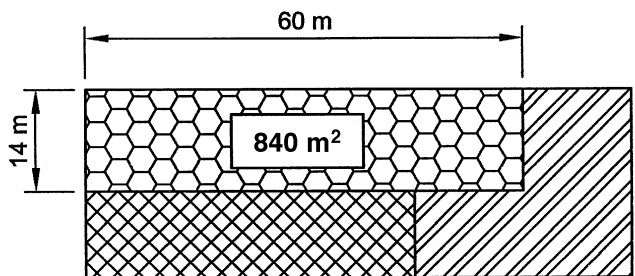


Fig. 15.10 Area required for a membrane (bipolar) plant.

If the choice is to utilise the full capacity of the existing rectifiers and install more membrane electrolyzers then adequate space is available. In the 200 000 tonnes per year example, utilising the voltage saved and adding 16 extra monopolar electrolyzers would take less space than the original diaphragm cells. In the case of bipolar electrolyzers, the length of the electrolyser could be increased as more anodes and cathodes are added to each electrolyser. The number of electrolyzers, however, would stay the same.

15.6 Utilisation of rectifier capacity

Going back to the original assumption of a 150 kA/450 V rectifier system, consider now the additional capacity that could be achieved by using the various membrane options available (Figs 15.11–15.13).



Fig. 15.11 Utilisation of rectifier capacity in diaphragm cells.



Fig. 15.12 Utilisation of rectifier capacity in monopolar membrane electrolyzers.

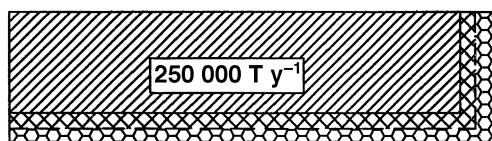


Fig. 15.13 Utilisation of rectifier capacity in bipolar membrane electrolyzers.

The monopolar option utilised 399 V (including bus bar losses) so an extra 16 electrolyzers can be added to the circuit making an extra 28 000 tonnes per year of caustic or US\$7 million extra sales value (at US\$250 per ECU). The bipolar option utilised only 360 V on each electrolyser so an extra 28 anodes could be added, manufacturing an extra 50 000 tonnes per year (Fig. 15.13). At US\$250 per ECU, this yields an additional US\$12.5 million of revenue.

Experience shows that diaphragm plant systems designed over 10 years ago can often handle extra volume with minimal changes owing to the generous design standards used at that time.

15.7 Partial and staged conversions

Where circumstances dictate, partial conversion of a diaphragm plant to membrane technology is possible (Fig. 15.14). The overall operating philosophy is to take the weak brine from the membrane electrolyzers, re-strengthen it, and feed it to the remaining diaphragm cells. This is usually the lowest cost option since a new brine plant, with recycled brine is not needed for a partially converted membrane plant. The weak brine would need to be dechlorinated prior to passing to the diaphragm plant for re-strengthening since brine vessels are mostly open-topped and noticeable gas releases would otherwise occur.

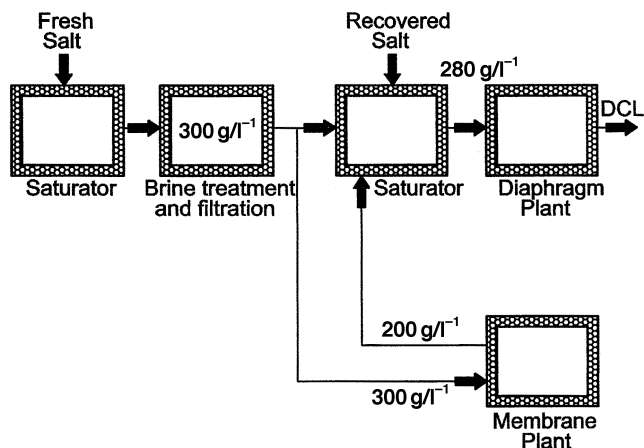


Fig. 15.14 Schematic of partial membrane conversion.

Owing to limitations on the water balance of the plant, a 40–50% conversion can be undertaken before a salt evaporator needs to be installed to remove excessive water. The feed brine for the membrane cellroom is taken from brine made from fresh imported salt and the weak brine is returned, combined with the diaphragm brine, re-strengthened with recovered salt from the evaporators and fed to the diaphragm cells. The concentration of brine to the diaphragm cells could be weaker than normal, at around $270\text{--}280 \text{ g l}^{-1}$ rather than $300\text{--}310 \text{ g l}^{-1}$ to assist with the water balance.

Staged conversions may also be carried out whereby a number of diaphragm cells is replaced with the equivalent number of membrane electrolyzers. For example, four diaphragm cells are removed, to be replaced by five monopolar membrane electrolyzers. A special switch would be required of, say, 20 V capacity to enable the work to be carried out with minimal loss of production. A special manifold header enables the pipe connections of the five membrane electrolyzers to be fed into the original four diaphragm cell flanges on the headers.

15.8 Electrolyser layouts

Replacement of diaphragm cells with monopolar membrane cells is straightforward in that it can be a one-for-one replacement, ending up with the same electrical circuit but accomplished in a shorter new length (see Figs 15.15 and 15.16).

Replacement of diaphragm cells with bipolar membrane electrolyzers requires a different electrical layout (Fig. 15.17) since each bipolar membrane electrolyser can only take about 17 kA of the 150 kA available (for a selected current density). This means that all nine electrolyzers need to be installed together. The number of anodes in each bipolar electrolyser can be set depending on the number of diaphragm cells left on load, up to the maximum voltage of the rectifiers.

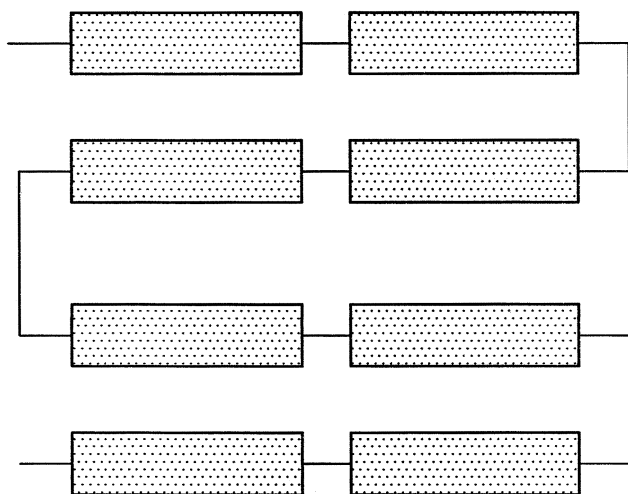


Fig. 15.15 Diaphragm cell layout.

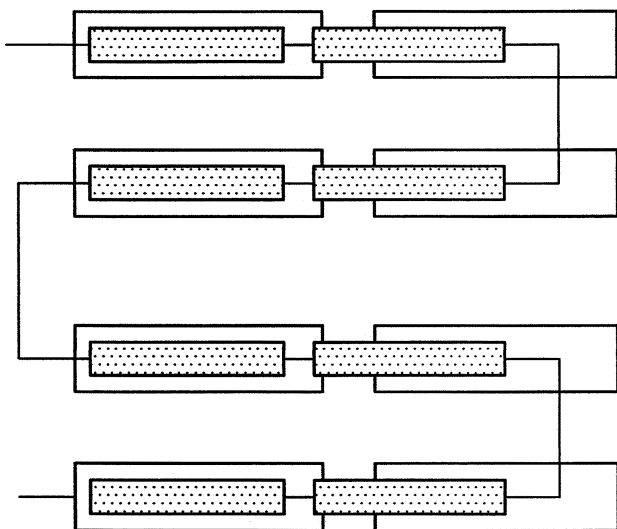


Fig. 15.16 Monopolar membrane electrolyser layout.

15.9 Caustic evaporation

The conversion of a diaphragm plant to membrane technology can utilise the existing diaphragm caustic evaporators. The duty is a lot less onerous in that instead of a 12% caustic soda solution in brine being fed to the evaporator there is now a 32% caustic solution in water. The salt removal equipment is redundant. An 18% increase in strength by the removal of water is simpler and less costly than a 38% increase in strength. Steam requirements are reduced significantly.

Partial conversions to membrane technology require some early decisions as to what to do with the product caustic soda. It is very easy to mix the membrane caustic

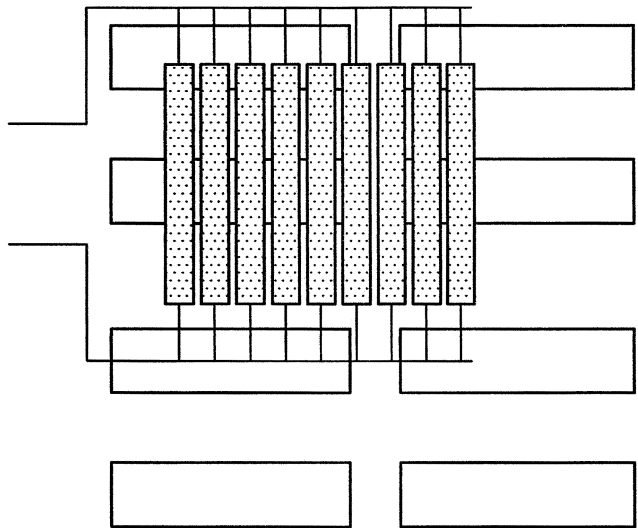


Fig. 15.17 Bipolar membrane electrolyser layout.

soda with the diaphragm caustic soda by feeding into the appropriate stage in the evaporator system. There is no capital cost for any extra equipment but this has to be balanced with the loss of all the extra value of the membrane caustic soda as it is blended into the diaphragm caustic soda.

Many caustic evaporator suppliers have schemes to separate the two types of caustic whilst making 50% solutions of both. A particularly good option is to install an extra first-effect evaporator for the membrane caustic soda and split the steam usage between the diaphragm first-effect and the new membrane first-effect, then recombine the steam again to feed to the rest of the diaphragm cell evaporator system.

15.10 Time considerations

Conversions of plants, be it partial, staged or complete takes some finite time to achieve. Prime consideration for producers is the occupancy of the existing plant during the project. A minimum occupancy will be set by the producer taking into account plant requirements and the needs of the market place. If the conversion is to be completed within the existing cellroom then a high occupancy requirement favours a staged conversion, replacing say four diaphragm cells at a time. A weak-priced market may favour a partial conversion which removes, say, 30% of the capacity whilst the conversion takes place. The time allowed for the conversion needs to be optimised for each client. Many factors come into play, such as the condition of the existing plant, but with careful planning a conversion can be achieved in weeks, rather than months.

If a completely new cellroom is being considered and space is available close to the

existing cellroom then the loss of production is determined by how long it takes to move the electrical feed from the old cellroom to the new cellroom.

15.11 Summary

It has been shown in this chapter that financial benefits result from the conversion of a diaphragm cellroom to membrane technology. Tonnage may be increased for a similar power consumption or power usage maybe decreased for the same amount of tonnage when a conversion takes place.

Taking the cost of a conversion of a 200 000 tonnes per year diaphragm plant to membrane technology at US\$50 million, it is now possible to look at what can offset this cost. The major diaphragm refurbishment cost of US\$7 million could be saved resulting in a cost differential, to access the benefits of conversion, of US\$43 million (see Table 15.1).

Table 15.1 Payback analysis of typical 200 kilotonnes per year diaphragm-to-membrane conversion.

Cash cost	
Cash in year of conversion	
Capital for conversion	\$50 million
Saving of refurbishment	\$7 million
Differential capital cost	\$43 million
Operational benefits (bipolar)	
Caustic soda price differential	\$2 million per year
Additional revenue from increased volume	\$12.5 million per year
Reduced steam usage	\$5.5 million per year
Total business benefit	\$20 million
Payback	43 years/20 = 26 months
Operational benefits (monopolar)	
Caustic soda price differential	\$2 million per year
Additional revenue from increased volume	\$7 million per year
Reduced steam usage	\$5.5 million per year
Total business benefit	\$14.5 million
Payback	43 years/14.5 = 36 months

However, the strongest argument when converting a plant is the consideration also of the option to manufacture more product for the same power cost of the original plant. In the case of bipolar technology, which in the example given here could add an extra 50 000 tonnes per year of caustic, it can be seen that at US\$250 per ECU this option earns extra revenue to the tune of US\$12.5 million per year. The reduction in steam usage from 2.1 to 0.7 tonnes per tonne gives a benefit, at US\$20 per tonne of steam, of a further US\$5.5 million per year.

A simple cash analysis for the 200 000 tonnes per year plant conversion is shown in Table 15.2. This analysis takes the prudent view that all of the conversion capital is spent up front.

It is possible to observe that a payback could be possible in three years after the

Table 15.2 Cash analysis of 200 kilotonnes per year conversion case (m = million).

Year	-1	0	1	2	3
Capital	– \$50m				
Refurbish		+\$7m			
Price differential			+\$2m	+\$2m	+\$2m
Extra production			+\$12.5m		
Reduced steam			+\$5.5m	+\$5.5m	+\$5.5m
Total	– \$50m	– \$43m	– \$23m	– \$3m	+\$17m

membrane plant has gone on load. Other benefits that have not been credited to the conversion case include the reduction of manpower, and improved customer confidence in their supply chain.

Not all diaphragm plants would consider conversion. In the case of plants where the diaphragm caustic soda from the cells is fed to a downstream plant there is no economic driver to convert. Indeed, ICI Chlor-Chemicals has a diaphragm plant where the sole requirement is the use of the diaphragm cell caustic as a reagent for treating raw brine for multiple chlor-alkali plants, ammonia soda plants and evaporated salt plants.

In conclusion the belief provided by this chapter is that the conversion of a diaphragm plant is a very practical proposition, providing a higher quality product and a payback over a very reasonable time period.

ICI Chlor-Chemicals Electrochemical Technology Business can provide the know-how, experience and membrane technology for any of the chosen options.

Chapter 16

Know-how and Technology – Improving the Return on Investment for Conversions, Expansions and New Chlorine Plants

R Beckmann and B Lüke

16.1 Preface

Krupp Uhde has more than 40 years of experience in the design and construction of chlorine/caustic soda plants [1]. The company's 150 plants throughout the world have an overall production capacity of approximately 8 million metric tonnes per year of NaOH (100%) and thus make Krupp Uhde unique in its field.

Research and development work on membrane technology was begun jointly with Hoechst AG, Bayer AG and Uhde GmbH in 1973 when the first commercial membranes became available. Until now, Krupp Uhde's know-how has been based on the combined efforts of these three companies in the research and development of this technology. One result is the Single Element patented in Europe in 1980 by Hoechst AG [2] followed by patent applications all over the world [3].

In 1998, Krupp Uhde became the sole owner of Single Element Technology and continues to put great effort into the further development of membrane cell technology for different electrolysis applications. With a new patent [4] for improved Single Element Technology, Krupp Uhde is ready for the future.

16.2 Introduction

Krupp Uhde (KU) know-how and technology is based on extensive experience in chlorine production and provides clients with short shutdown periods for the conversion of chlorine plants to membrane technology, low-energy consumption and includes special technologies for higher chlorine quality and hydrogen-free production.

This technical leadership together with the Krupp Uhde know-how and the licence for the membrane process – which makes Krupp Uhde the only licensor and contractor able to supply complete plant complexes from one source – is the basis for the ongoing success of Krupp Uhde Single Element Technology for electrolysis applica-

tions. This can be illustrated by an example of the profitability for investments – the return on investment (RoI) [5].

The return on investment is derived from the ratio of the total capital invested and the turnover to profit:

$$\text{RoI} = (\text{profit/turnover}) \times (\text{turnover/capital invested})$$

The RoI is used in the analysis of profitability that represents the ratio of a profit figure to the capital employed in an accounting period, the two figures being assessed by balancing. Compared with other profitability analyses, the RoI consists of *two* indices that assess the success of an investment: the profit–sales ratio and the ratio of sales to the total capital employed. The RoI can serve as the basis for company policy and company budgeting. When used as a decision criterion, the static scrutinising method causes this return to be related to a given moment of time.

Using the Krupp Uhde know-how and technology an improvement of *both* RoI indices is achieved as a result of the shorter shutdown periods for plant conversions and expansions and the short engineering and construction periods for new plants by virtue of the fact that Krupp Uhde functions as a general contractor. Coupled with the use of the Krupp Uhde Single Element Technology for high-quality products with low energy consumption, the indices for the profit–sales ratio and the ratio of sales to the total capital employed are noticeably improved owing to higher profit for the products, less capital invested and an increased turnover. Krupp Uhde know-how and technology is elucidated in the following sections on the basis of different practical examples.

16.3 Performance of the new Krupp Uhde Single Element

The heart of an electrolysis plant is its electrolyzers. The factors that improve the RoI are features such as low energy consumption and high on-stream factors, flexibility of plant load, high current densities and short electrolyser downtime periods for maintenance.

Figure 16.1 illustrates the low level of energy consumption of a Krupp Uhde plant equipped with the new KU elements on the basis of the anodic balance, the plant being operated at 4 kA m^{-2} and the brine being acidified. The graph, which covers a period of over two years, is characterised by a low rate of increase of the original value of 2030 kWh per tonne of NaOH. The graph was confirmed by an efficiency test conducted in July 1999, on the basis of the caustic solution produced, which yielded an energy consumption of 2105 kWh per tonne of NaOH.

This means that the figure of 2130 kWh/t/NaOH at 5 kA m^{-2} as quoted in literature [6] is even higher than the value reached with KU elements in the first months of operation and that the new KU single element provides low energy consumption.

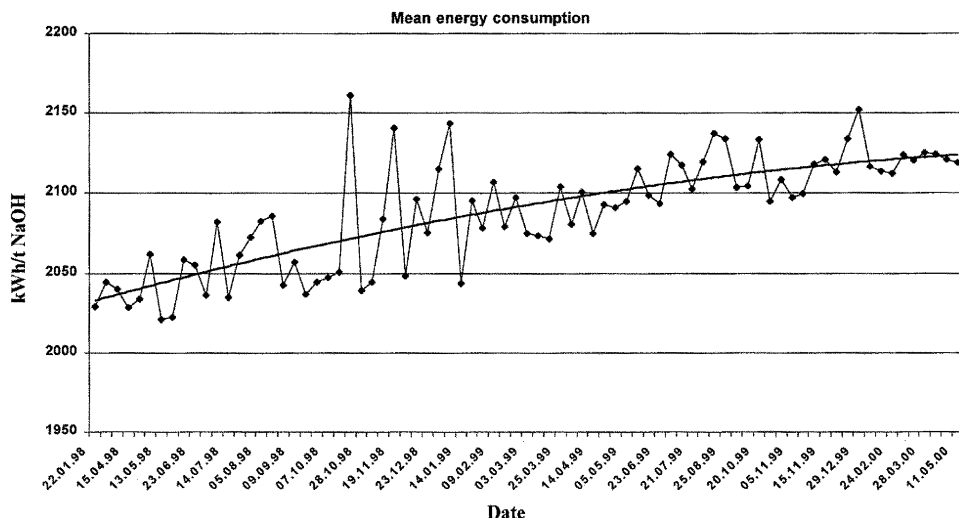


Fig. 16.1 Mean energy consumption of a 125 000 metric tonnes per year NaOH plant according to the anodic balance and with brine acidification.

Load tests in Krupp Uhde's own high-performance test bay at Gersthofen, Germany, demonstrate the high efficiency of the new KU single element (Fig. 16.2). The almost linear current–voltage curve up to a current density of 8 kA m^{-2} proves the high efficiency of the internals and improvements in the new KU single element generation [4]:

- minimum concentration differences in the cathode and anode chambers
- minimum contact and structural losses
- homogeneous current density distribution.

A typical example of the continual improvement of this top-ranking single-element technology is the further optimisation of the time-proven downcomer [7] (see Fig. 16.3).

The louver structure of the anode patented by KU [8] is highly suited for amalgamating the electrode and downcomer to a single design element. By inclining the louver structure against the horizontal, a preferential flow is imparted to the chlorine gas emanating from the anode, thus causing the anolyte to circulate along the anode structure without an additional downcomer plate.

Tests with these inclined louvers [9] (Fig. 16.4) showed that the cell voltage dropped, this drop being more prominent (see Fig. 16.5) with an increasing current density, as was expected. This suggests that this innovation of the anolyte circulation acting upon the anode not only lowers the energy consumption but also lowers the material costs for the cell because no specific internals are required and manu-

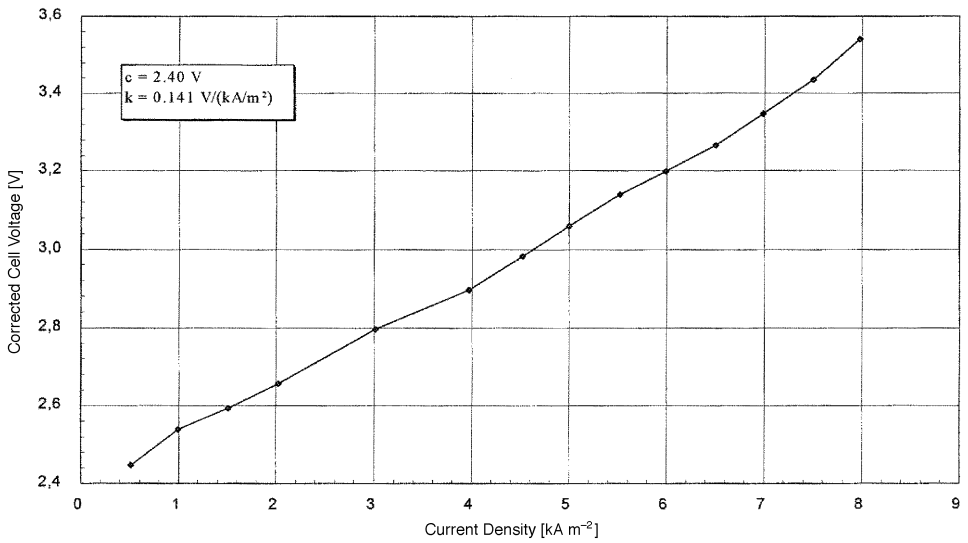


Fig. 16.2 Current-voltage curve of the latest KU single element in the high-performance test bay (eight elements) at Gersthofen, using an N981 membrane from DuPont.



Fig. 16.3 Downcomer principle in the latest KU single-element design.

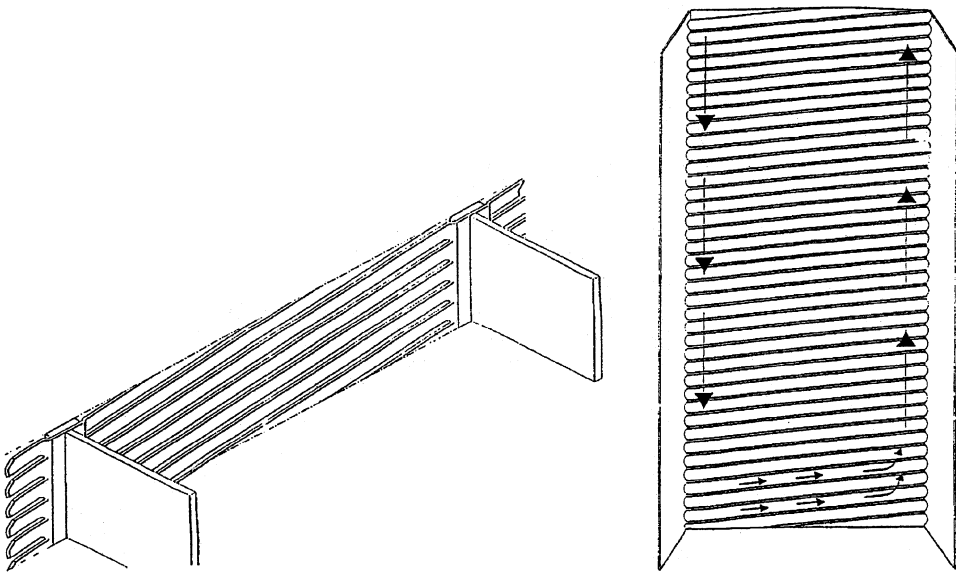


Fig. 16.4 Functional diagram of the inclined louvers in the web area of the KU single element.

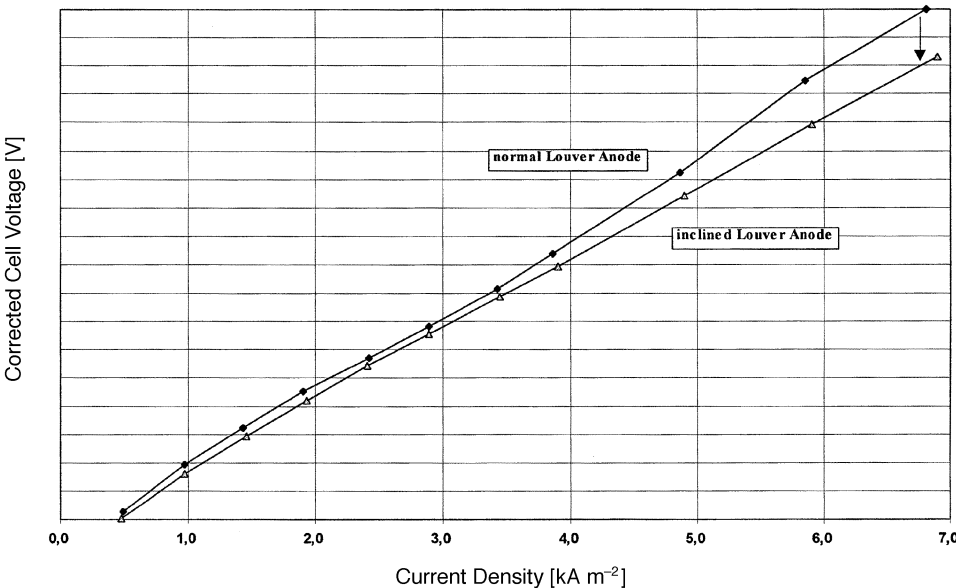


Fig. 16.5 Current-voltage curves with normal and inclined anode louvers showing a cell voltage decrease when using inclined anode louvers.

facturing of the cell becomes simpler. The release for industrial application of the KU single element is expected for end of the year 2000.

All these modifications lead to the fulfilment of all aspects for an improvement of the RoI by KU single element technology and high efficiency of the latest cell design, such as low energy consumption with a high on-stream factor for the plant, simple and rapid maintenance of the electrolyzers, plant load flexibility and high current densities.

16.4 Conversion, expansion and new chlorine plants

An improvement of the RoI for the conversion and expansion of existing and new chlorine plants is achieved by the high flexibility of the electrolyser technology and by employing a modular principle for the plant or electrolyser concept, a major role being played by short shutdown periods and a current density that is adapted to the client's requirements. This is where single-element technology and the modular construction of the electrolyzers enable KU to offer high flexibility and adaptability to the particular local conditions: this is aptly demonstrated by the latest conversion contract – hitherto the largest in Europe – awarded to Krupp Uhde.

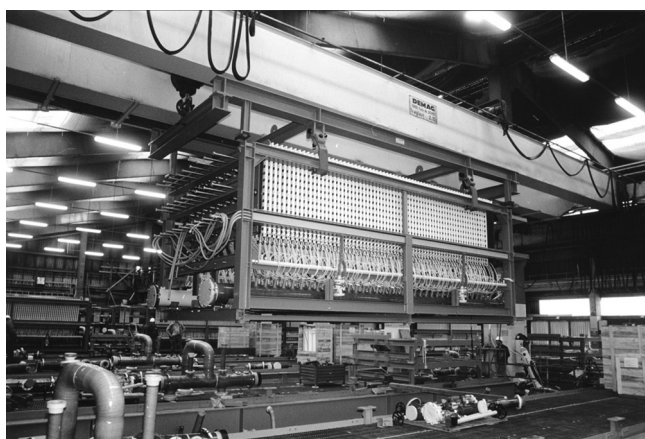
As a result of KU's know-how in this field, the guaranteed shutdown period for converting a 340 000 metric tonne per year NaOH plant from mercury to membrane technology was as short as 8 weeks. This was made possible by a new conversion concept: the individual elements were assembled in an adjoining assembly hall and installed in cell racks of 72 elements each. In this way, more than 2600 elements were assembled and installed in 18 two-rack electrolyzers, and pressure and leakage tested. As soon as part of the mercury electrolysis plant was dismantled, the completed electrolyzers were placed onto the vacated area and connected to the piping already installed beneath the cell rows (Fig. 16.6).

The adaptation of the current density of new membrane electrolyzers to the existing transformer/rectifier units is an integral part of KU engineering and is carried out with due consideration to all individual costs of the cellroom, so that the profitability of the plant with the new transformer/rectifier units as opposed to the existing units can be determined on the basis of the optimum current density. Figure 16.7 is a plot illustrating the example of a 50 000 metric tonnes per year NaOH plant showing minimum total costs at a current density of 4.95 kA m^{-2} based on figures of $0.04 \text{ euro kWh}^{-1}$ for electricity, 8 years' depreciation and 8% interest on the capital invested.

In general, it can be said that minimised production costs will be found when the current densities are higher and the cost of electricity and the k-factor value of the current-voltage curve for the technology employed are lower. With the low k-factor value shown above for KU single-element technology and the option for high current densities, KU provides for minimum production costs, thus making for higher profits and, consequently, improving the RoI.



(a)



(b)

Fig. 16.6 Transport and installation of completely pre-assembled electrolyzers with 72 single elements as part of the new KU conversion concept.

Another example of different conversion concepts is given by a study of the conversion of a diaphragm electrolysis plant to KU membrane technology, the overall plant capacity being affected to the extent of only a small degree during the conversion phase by employing step-by-step conversion (see Figs 16.8 and 16.9). Here, too, optimum flexibility and adaptation to the local conditions with minimum space requirements for the KU electrolyzers is achieved by the KU single-element technology and the modular construction of the electrolyzers, thus minimising the costs and the duration of the plant conversion and expansion.

16.5 Improved product quality

An improvement of the RoI can also be achieved by an improved product quality, if the market allows higher sales of, or higher profits for, the chlorine/NaOH product. To this end, KU provides know-how and experience in the field of pure brine acidi-

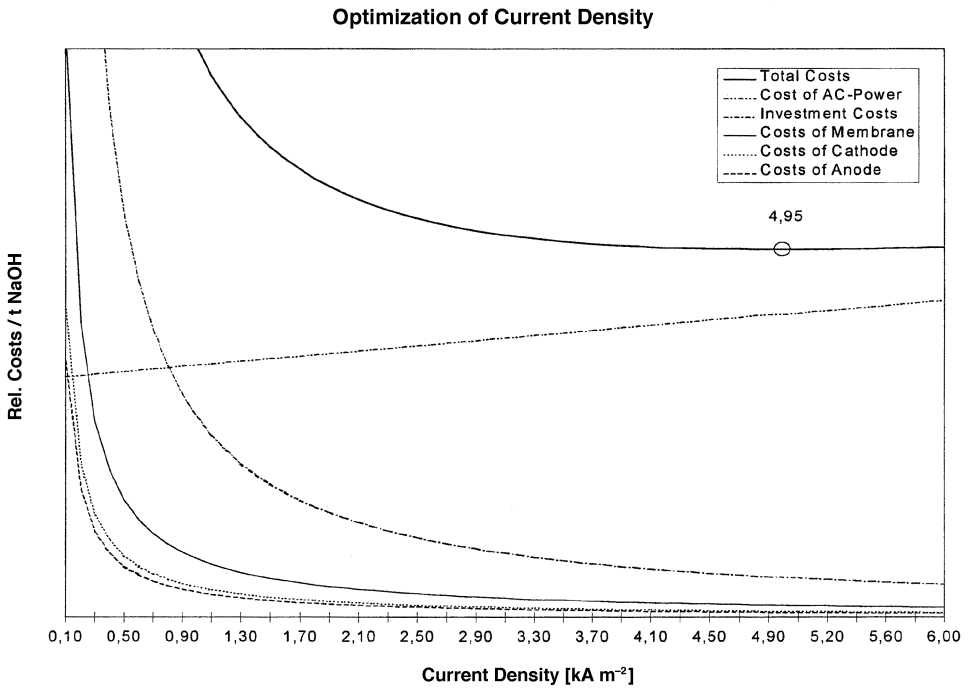


Fig. 16.7 Relative costs for a 50 000 metric tonnes per year NaOH plant as a function of the current density. Only the costs of the cellroom and rectifier were taken into account.

Membrane electrolysers	0	0	5	10	15
Diphragm-cells	160	128	76	0	0
tpd Cl ₂					(900)
900					
800					
700				(600)	
600	(600)		(585)		
500		(480)			
400					
300					
200			(300)		
100					
Phase	0	1	2	3	4

Fig. 16.8 Conversion and expansion of a 600 metric tonnes per day chlorine plant in four steps to a plant capacity of 900 metric tonnes per day using KU single-element technology.

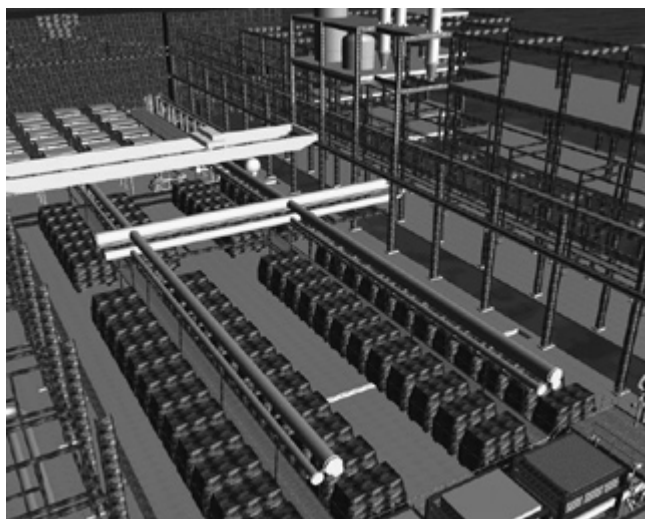
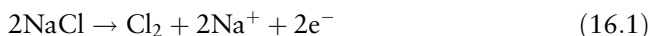


Fig. 16.9 Conversion and expansion of a 600 metric tonnes per day chlorine plant in four steps to a plant capacity of 900 metric tonnes per day using KU single-element technology (phase 2).

fication which lowers the oxygen content of the chlorine by 1–2.5% (v/v), increasing over time, to approximately a constant 0.6% (v/v) in normal operation. The acidification principle is based on electrochemical laws. The normal anode reaction is the chlorine evolution reaction according to the following equation:



The voltage of the above reaction under standard conditions is 1.35 V. A competing reaction at the anode is the oxygen evolution reaction according to the following equation:



The voltage of the oxygen evolution reaction under standard conditions (pH = 0) is 1.23 V. As the potential for oxygen evolution (Equation 16.2) is lower than the potential for chlorine evolution (Equation 16.1), oxygen evolution at the anode will always take place to some extent.

There are several methods for reducing the oxygen content of the chlorine gas. These are mainly:

- (1) Improvement of the anode coating and structure. The purpose of this measure is to achieve a higher overvoltage of oxygen evolution and a lower overvoltage of chlorine evolution in order to overcome the potential difference between the two electrochemical reactions at the lowest possible current densities. This will reduce the fixed portion of oxygen evolving at the anode.
- (2) Lowering the pH value. As the anodic reaction of chlorine evolution proceeds

independently of the pH value and the oxygen evolution depends on the pH value (1.23 V for pH = 0 and 0.40 V for pH = 14), the potential of the oxygen evolution increases with a low pH value, thus reducing the extent of oxygen evolution according to the overvoltage ratio of the anode, and this results in an improvement of the chlorine quality. Furthermore, less hypochlorous acid will be formed at lower pH in the anode compartment due to the caustic arriving from the cathode side being neutralised and hence the oxygen formed from the decomposition of the hypochlorous acid is noticeably reduced.

KU is working on both of these points to improve the chlorine quality. Point (1) is continually being optimised jointly with the coating manufacturers, with whom KU maintains close liaison. Figure 16.10 plots the acidification results in an operational plant and represents the optimisation of point (2). The quantity of hydrochloric acid used is as low as 18–20 kg per tonne of NaOH leading to an anolyte pH of 2.4–2.8 and an oxygen content in chlorine gas of 0.5–0.8 vol. %.

Plotting the oxygen content measured at a current density of 4 kA m^{-2} versus the measured anolyte pH, the relationship as shown in Fig. 16.11 is obtained as expected. This proves again the high internal anolyte circulation of the KU Single Element that makes possible an oxygen content of 0.6% in chlorine at an anolyte pH of only 2.5.

Another factor contributing to higher profitability is the fact that should the electrochemical side-reaction of oxygen evolution is reduced by about 1%, the

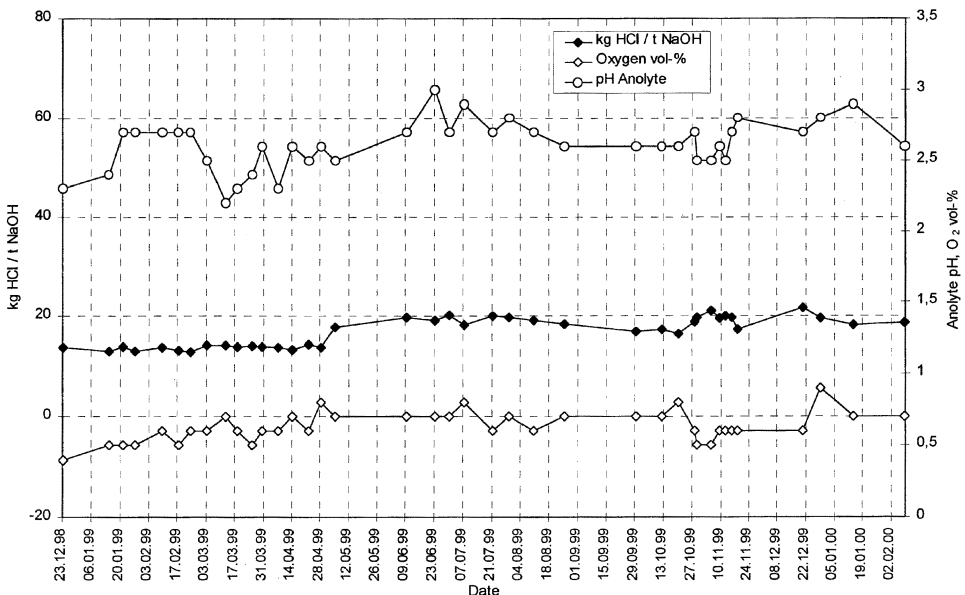


Fig. 16.10 Achievable oxygen content in chlorine gas from an electrolyser (158 elements) versus the anolyte pH and the HCl quantity used (100%) per tonne of NaOH.

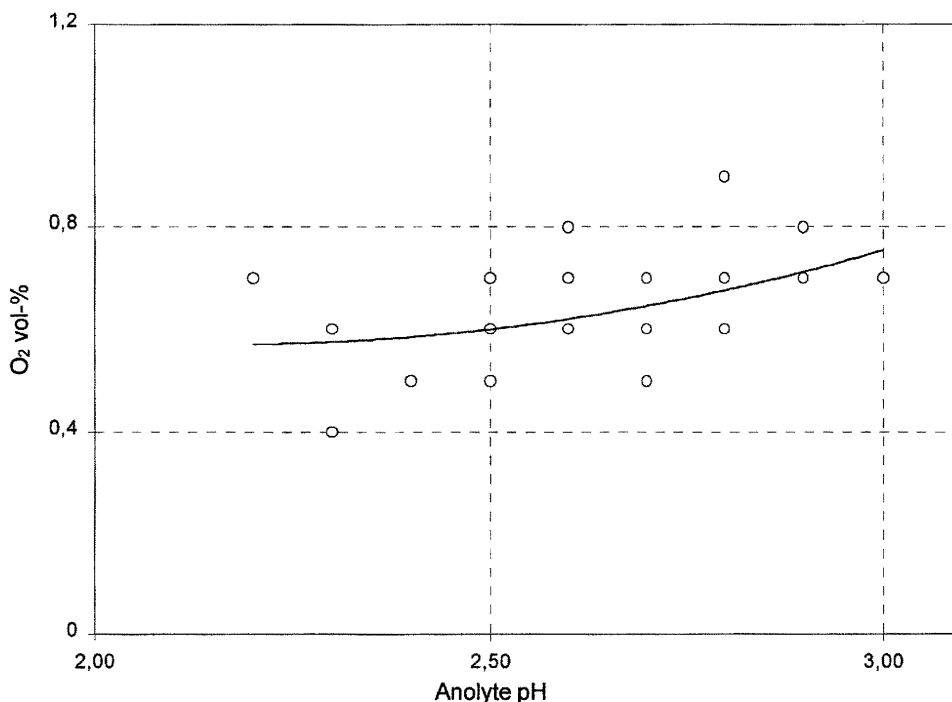


Fig. 16.11 Oxygen content of chlorine versus anolyte pH of the latest KU single-element generation (accumulated over more than one year of operation).

chlorine quantity evolving at the anode will be about 2% higher as a result of brine acidification as compared with a plant not using acidification but chlorate decomposition instead. In this way, the prerequisites for improving the RoI are created with the aid of KU know-how and technology by exploiting the possibilities of improving the product quality.

16.6 New cell design and technology

In order to increase the superior position that KU single-element technology has on the market, KU is not only engaged in intensive research and development for continual improvement of the existing electrolyser technology, but is also investing in future technologies. The aim is to lower substantially the specific energy consumption in a chlorine production plant. KU is basically pursuing two methods to achieve this, namely a new electrolyser design and new electrode technologies. These are detailed below.

- (1) KU holds the patent for a new electrolyser technology, the falling film electrolyser [10] (FFE; see Fig. 16.12), with an expected lowering of the cell voltage of

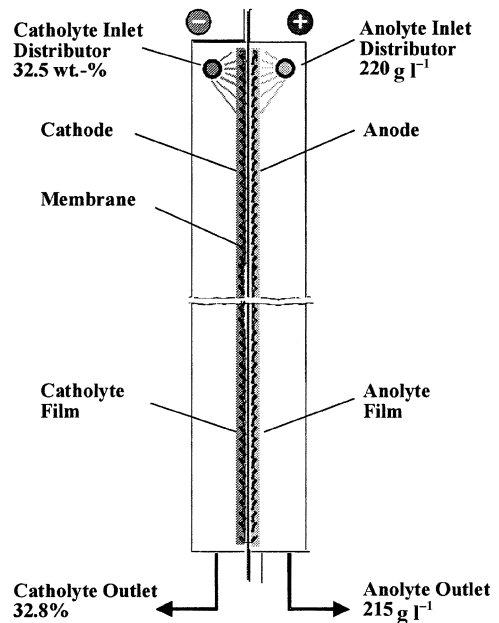


Fig. 16.12 Principle and advantages of the falling film electrolyser. Advantages include: improved mass and heat transfer; low gas content in electrolyte; low concentration difference; constant hydraulic pressure; low expected voltage of 2.70 V at 3 kA m^{-2} leading to power consumption reduction of 70 kWh per tonne of NaOH at 4 kA m^{-2} , including circulation pumps; and small element depth.

2.70 V at 3 kA m^{-2} . Compared with the latest KU single element, the power consumption – considering additional circulation pumps – will be reduced by 70 kWh per tonne of NaOH at 4 kA m^{-2} .

- (2) Incorporation of oxygen-consuming gas-diffusion electrodes (GDE) in the falling film electrolyser (Fig. 16.13) for hydrogen-free chlorine electrolysis facilities will result in an expected lowering of the cell voltage by 0.9 V as compared with the latest KU electrolyser generation.

KU, in co-operation with a German battery manufacturer, managed within a short time to produce silver GDE with a low PTFE content and to adapt them to the chlor-alkali technology in test cells. An examination of the GDE manufactured using a special process shows that the active silver centres of the GDE are held together by PTFE filaments in the form of a spider's web (Fig. 16.14).

The cell voltages in KU test cells on GDE with silver catalyst are of the order of 1.9–2.0 V under standard conditions. Assuming similarly good k -factor values of the FFE with GDE and of FFE without GDE, the energy consumption will be as shown in Fig. 16.15.

On this basis KU is already in a position to determine with its clients the profitability of a conversion of an existing plant to GDE cathodes or the equipment of new plants with such cathodes, taking into consideration the price of electric energy, the cost of industrial oxygen and a compensation for the absent hydrogen. Figure 16.15 illustrates aspects such as re-membraning combined with the installation of a new

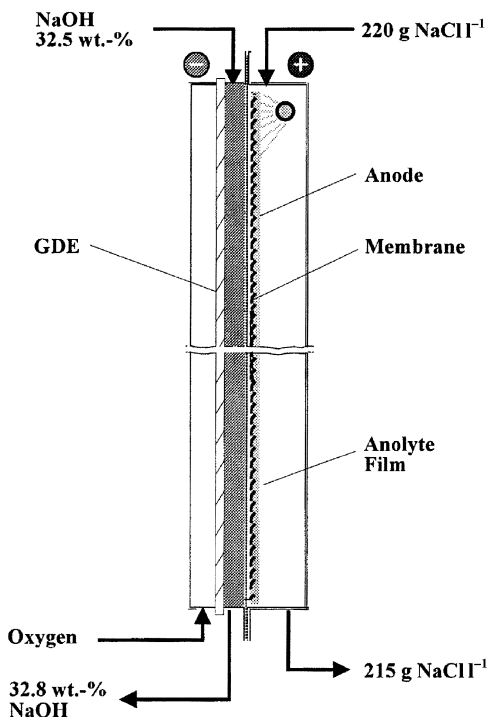
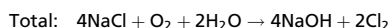
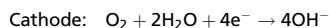
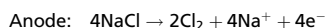


Fig. 16.13 Adoption of GDE technology in a falling film electrolyser with modified cathode reaction. Reactions are:



The principal advantage of the technology is the low cell voltage and therefore low specific power consumption.

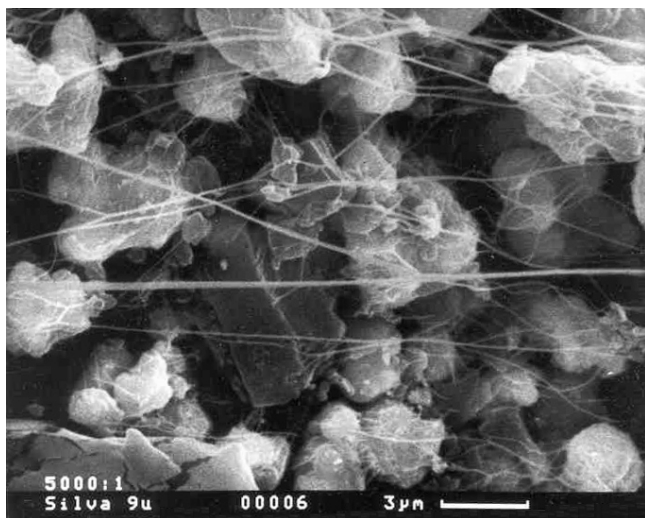


Fig. 16.14 Enlargement ($\times 5000$) of a silver GDE with silver catalyst and low PTFE content.

GDE or a comparison of the service life of a GDE with the total life of a cathode coating.

With the FFE patent and the know-how for the manufacture of the SILFLON electrode (a silver GDE with low mercury content of about 3%) developed by Hoechst AG, KU is in a position to draw upon the experience and the results of test

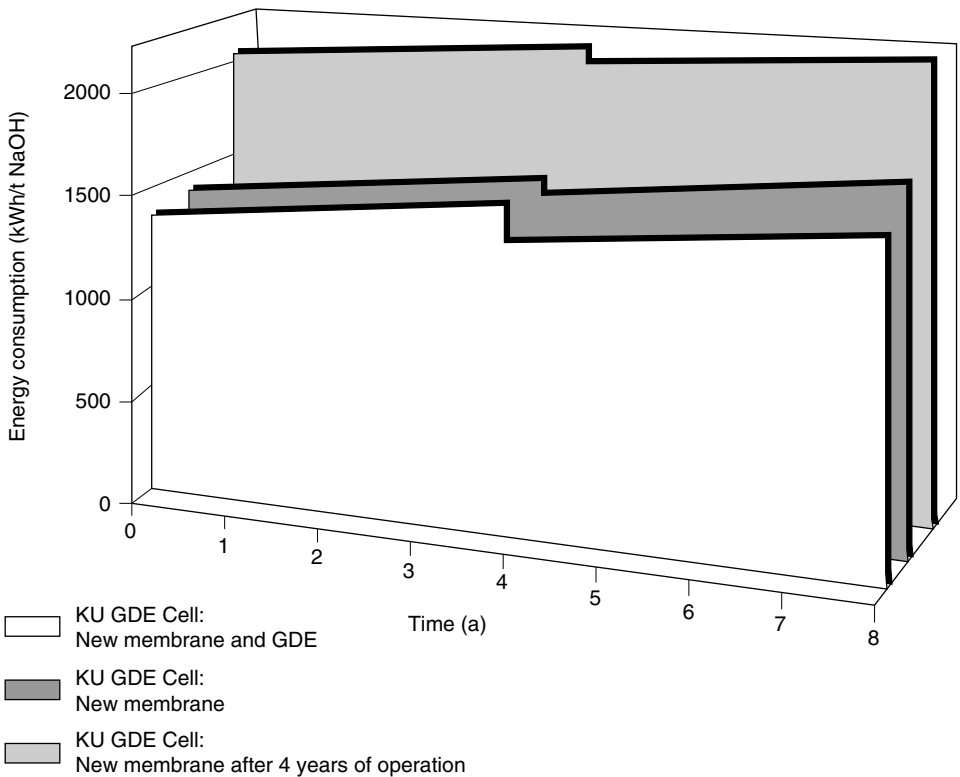


Fig. 16.15 Comparison of the specific energy consumption versus time of KU electrolyzers of the latest generation and the latest KU GDE cell at 4 kA m^{-2} . Only the increase due to the membrane and cathode is taken into account.

operations conducted over a period of three years. Thus, KU occupies a leading position in providing the technology for the use of GDE in chlor-alkali electrolysis plants.

The calculations on the profitability of GDE technology suggests that the use of GDE might be worthwhile even with an electricity price of $0.05 \text{ euro kWh}^{-1}$, if the calorific value of hydrogen is taken into account on the credit side. If the electrolysis hydrogen permits higher prices to be realised, for instance when used as synthesis gas, the profit achieved with hydrogen-evolving KU technology will be higher still.

If the hydrogen is released into the atmosphere, a conversion to GDE will be profitable down to an electricity price level of $0.025 \text{ euro kWh}^{-1}$. In general, it can be said that a conversion to GDE cathodes will be the more interesting for all applications the higher the electricity price is above this lower limit of $0.025 \text{ euro kWh}^{-1}$.

The GDE for chlor-alkali electrolysis plants is still a relatively new concept compared with other chlorine technologies. It may be assumed that there is still considerable development potential in this newer technology. The above cost and RoI figures are based on optimistic values and should be regarded as provisional. In

industrial-scale tests at Gersthofen, Germany, KU is proving the long-term reliability of this technology.

16.7 Data processing and analysis – new database combined with neuronal nets

All aspects of electrolysis plant operation can be completely covered with the aid of a new database for recording all electrolyser data (Fig. 16.16). KU is for the first time able to apply new technologies, such as neuronal nets. This is being undertaken in co-operation with the University of Münster, Germany.

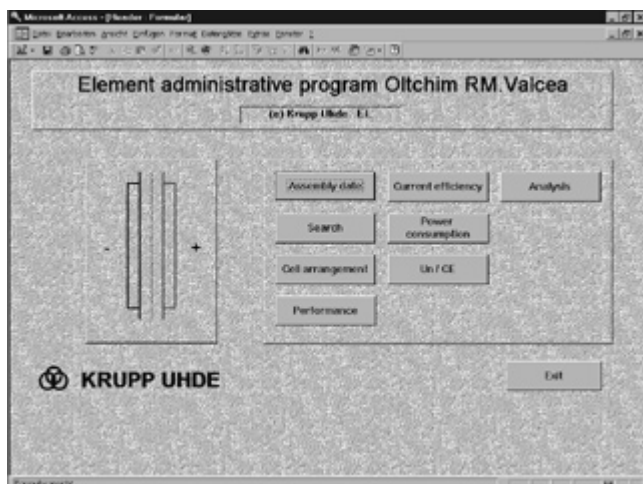


Fig. 16.16 Element management program for Krupp Uhde chlorine plants.

Modern data acquisition and evaluation help to optimise the plant under review within a short period of time, to eradicate faults in plant operation and to determine the best materials for the operation of the chlorine electrolysis plant being examined. In this way, inter-relationships are examined between the energy consumption and variables such as membrane types, anode and cathode coatings, temperature, pressure, and concentrations as well as plant shutdowns, brine impurities, materials of construction and manufacturers. It is conceivable that other inter-relationships will come to light that have so far not been considered.

A data analysis example, such as that shown in Fig. 16.17, permits an assessment of different membrane types, and anode and cathode coatings with regard to the cell voltage from studies of more than 1900 single elements at standardised conditions.

All these findings will ultimately lower operating costs, and thus improve the RoI. KU is presently handling the task of creating the database to record these findings.

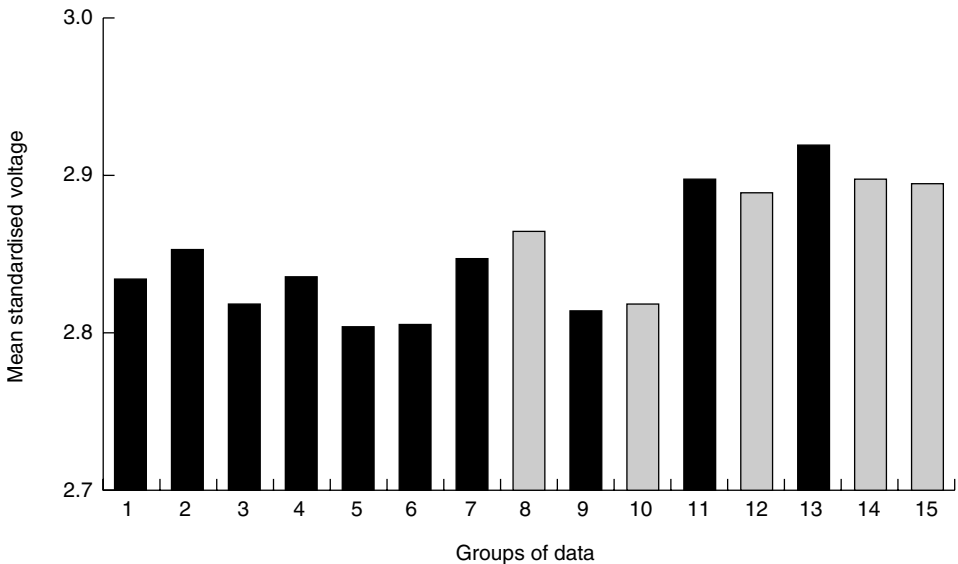


Fig. 16.17 Data analysis of more than 1900 single elements with regard to the standardised voltage for different groups of membrane types, and anode and cathode coatings.

16.8 Discussion

All the examples quoted show how costs can be lowered, profit for products increased and the turnover enlarged by selecting KU know-how and technology for chlor-alkali electrolysis plants.

The use of Krupp Uhde know-how and technology improves *both* indices of RoI. The shorter the shutdown periods for plant conversions and expansions, the shorter engineering and construction periods for new plants, by virtue of Krupp Uhde's ability to offer complete plants from one source, combined with the use of the Krupp Uhde Single Element Technology for high-grade products with low-energy consumption and the development and application of new technologies drastically improves the RoI indices of profit-sales ratio and the ratio of sales to the total capital employed.

With Krupp Uhde know-how and technology, new plants and conversions, future-oriented technologies, after-sales service and plant monitoring are all offered with increased profits on products, reduced capital expenditure and increased turnover converging to an improved RoI.

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Chapter 17

New Electrolyser Design for High Current Density

Y Takahashi, H Obanawa and Y Noaki

17.1 Introduction

Advances during the past 20 years in membrane, electrolyser, electrode, and brine purification technologies have substantially raised the performance levels and efficiency of chlor-alkali production by ion-exchange membrane electrolysis, bringing commercial operations with a unit power consumption of 2000–2050 kWh per ton of NaOH or lower at 4 kA m^{-2} current density with a membrane life of four years or longer.

The quest for higher efficiency and lower production cost is now leading inevitably to the development and adoption of larger electrolyzers and higher current densities. As indicated from the calculation of optimum current densities at given electric power costs illustrated in Fig. 17.1, the optimum current density at a unit power cost of

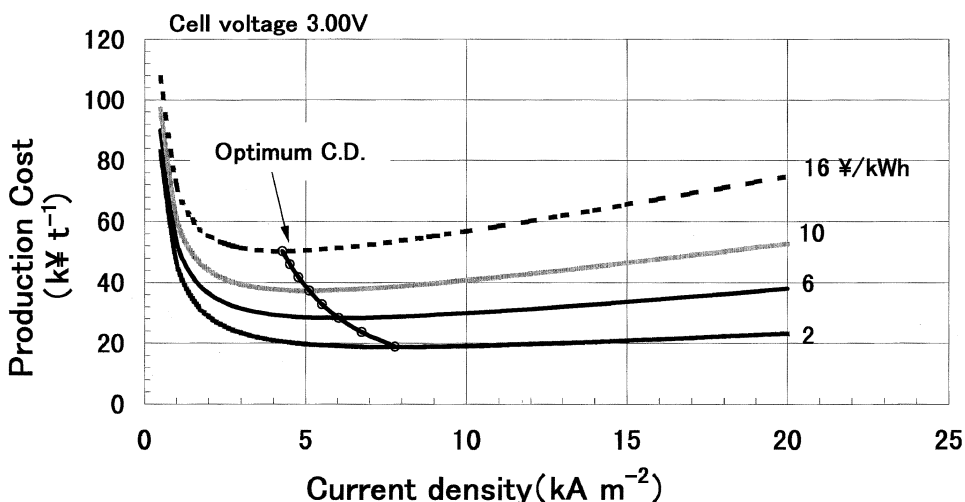


Fig. 17.1 Optimum current density for low production cost at given power cost.

$\approx 6 \text{ kWh}^{-1}$ and a cell voltage of 3.00 V is 6 kA m^{-2} or more. If the cell voltage can be lowered, moreover, the optimum current density becomes even higher.

Research and development in electrolyzers and membranes is in progress to meet the requirement for large-scale electrolyzers and higher current densities, and to resolve the questions relating to the effect of operation at 6 kA m^{-2} and higher on-membrane performance and service life, in contrast to the widely known performance and reliability as proven through many years of operation at 4 kA m^{-2} .

Asahi Chemical is now in the final stages of its programme of electrolyser development for stable long-term operation at these higher current densities, based on an extensive investigation of the related electrolysis characteristics. This chapter describes Asahi's findings, and particularly their effects on the intramembrane Na^+ concentration profile, and the structure of the new electrolyser design based on these findings.

17.2 Current state of the membrane process

As indicated in Fig. 17.2, the membrane process has long been characterised by substantial reductions in electric power consumption, through constant advances in membrane, electrolyser and electrode technologies. In the early years of its commercial establishment, some 25 years ago, it yielded a caustic soda concentration of 20% or lower, with less than 90% current efficiency. Today, the caustic soda concentration is 33%, the current efficiency is 97%, and the ohmic drop of the membrane has been lowered by approximately 1.0 V. During the same period, advances in electrolyser design have improved the uniformity of intracell electrolyte concentra-

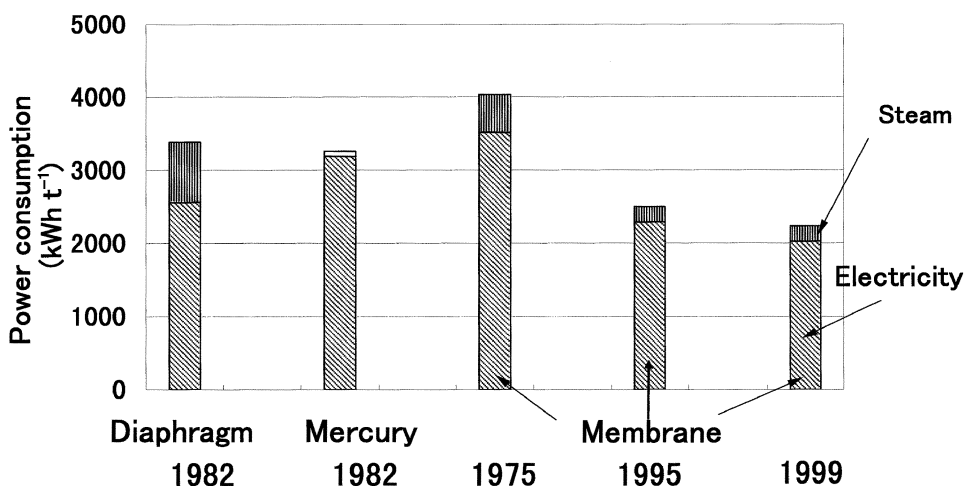


Fig. 17.2 Unit energy consumption of membrane, diaphragm, and mercury processes.

tions and narrowed the electrode gap, thus reducing the ohmic loss in the electrolytic solutions by more than 30%. Advances in electrode design and composition have also contributed to a reduction in power consumption. The replacement of steel cathodes with activated cathodes, in particular, has brought a reduction of more than 250 mV in cell voltage.

To date, as indicated in Fig. 17.3, the effort to reduce cell voltage has been focused on the membrane and the electrodes. In current commercial operations at 4 kA m^{-2} with a 2 mm electrode gap, the voltage loss of the membrane, anode and cathode has been reduced to approximately 350 mV, 50 mV and 100 mV, respectively, and thus a total of approximately 500 mV for these cell components, or less than one-third the voltage loss of these components in the early years of the commercial membrane process.

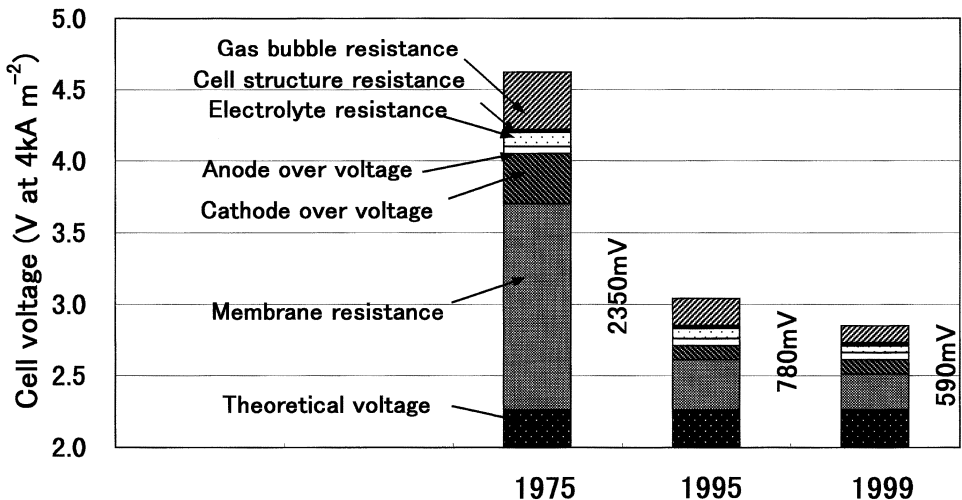


Fig. 17.3 Components of cell voltage, 1975–1999.

One remaining area of electrolyser development which will permit substantial reductions in cell voltage is the electric resistance of the electrolyte solutions and the gas bubbles located between the two electrodes. In present commercial electrolyzers, the voltage loss due to these factors is estimated to be approximately 100–200 mV while operating with an electrode gap of 2 mm. Development of the zero-gap cell and other modifications in the electrolyser structure, electrode configuration and electrode gap is now in progress to reduce the influence of electrolyte solutions and gas bubbles and thereby further lower the electrical resistance of these components, which will become increasingly important for membrane process operation at higher current densities.

17.3 Effects of operation at high current density

Membranes and electrolyzers from Asahi Chemical have been developed and produced in a comprehensive range. The two basic membrane categories are the Aciplex F-2000 series, for 23% caustic soda, and the Aciplex F-4000 series, for 30–33% caustic soda. As shown in Fig. 17.4, the continuing development of the F-4000 series has brought significant reductions in ohmic drop and other characteristics of membrane performance. All of these membranes are designed for a broad range of electrolytic conditions, including pressurised and non-pressurised operation, and operation with or without addition of hydrochloric acid to the feed brine. The electrolyzers, as indicated in Table 17.1, have also been developed and are designed for a broad range of operating conditions, ranging from forced-circulation pressurised operation to natural-circulation normal-pressure operation. Operation at current densities of 6 kA m^{-2} and higher, however, will impose a new set of requirements, for both the membranes and the electrolyzers.

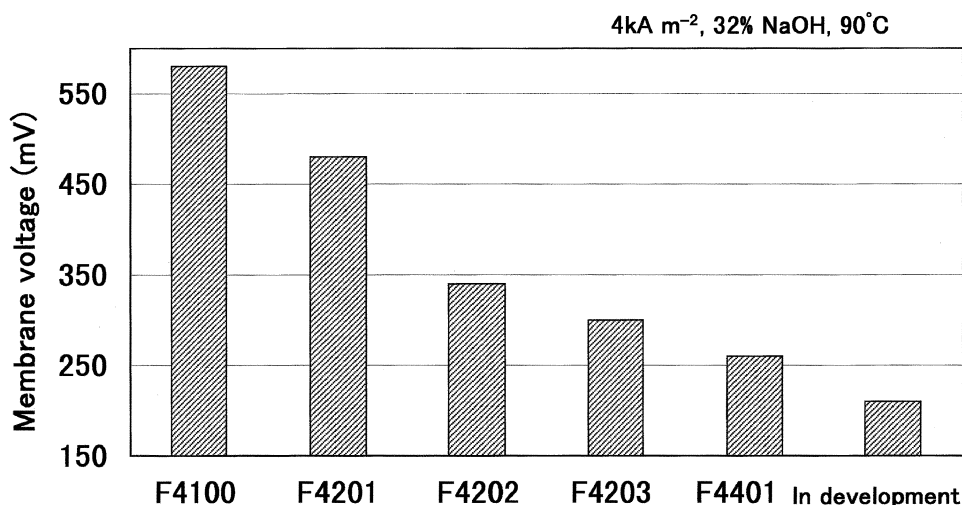


Fig. 17.4 Course reductions in membrane ohmic drop.

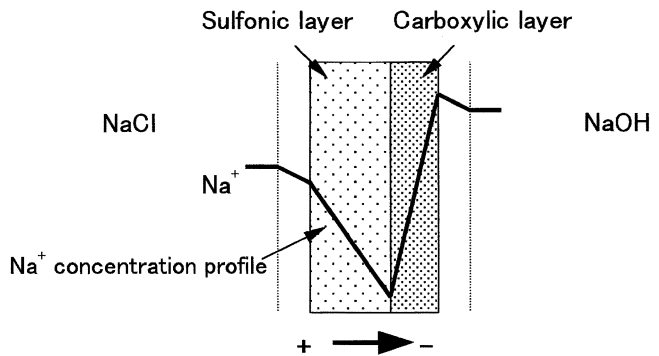
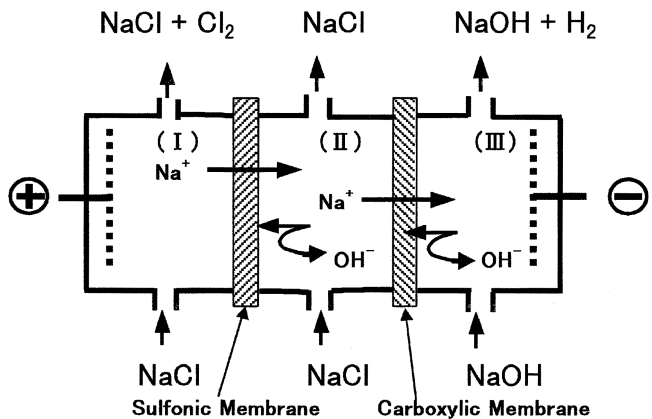
17.3.1 Intramembrane Na^+ concentration profile

Ion-exchange membranes for chlor-alkali electrolysis generally contain a sulphonic layer which faces the anode and a carboxylic layer which faces the cathode, joined by lamination. The Na^+ transport number is higher in the carboxylic layer than in the sulphonic layer, and a region of low Na^+ concentration therefore tends to form at the interface between the two layers during electrolysis, as shown in Fig. 17.5.

Asahi Chemical has investigated the effects of this low-concentration region on the membrane performance using the three-compartment cell shown in Fig. 17.6, which

Table 17.1 Basic operating parameters of electrolyzers from Asahi Chemical.

Electrolyser	Circulation	Cell pressure (kPa)	Effective surface area (m ²)	Maximum current density (kA m ⁻²)
ML32FC	Forced	50–100	2.7	4.5
ML60FC	Forced	50–100	5.0	4.5
ML32NC	Natural	10–80	2.7	5.0
ML60NC	Natural	10–80	5.0	5.0
ML32NCH	Natural	10–80	2.7	8.0
ML60NCH	Natural	10–80	5.0	8.0

**Fig. 17.5** Na⁺ concentration profile in ion-exchange membrane and vicinity.**Fig. 17.6** Three-component compartment laboratory cell.

consists of an anolyte compartment (I), an intermediate compartment (II), and a catholyte compartment (III), with a sulphonic membrane separating compartments I and II and a carboxylic membrane separating compartments II and III.

Asahi's investigations showed that a Na⁺ concentration of 1.1 N was necessary in compartment II to maintain a current efficiency of 96% in the carboxylic membrane during operation with 3.5 N brine in compartment I and 32% caustic soda in compartment III. The Na⁺ concentration in compartment II was generally far lower than that in compartment I, and clearly indicates the tendency for depression of the Na⁺ concentration at the interface of the sulphonic and carboxylic layers in the normal

membrane to a level substantially below that in the anolyte compartment. As shown in Fig. 17.7, operation of the three-compartment cell with various brine concentrations in compartment II clearly showed that reducing the concentration in compartment II results in a corresponding fall in current efficiency.

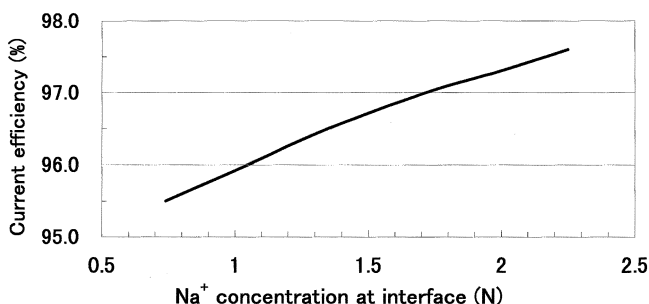


Fig. 17.7 Influence of Na⁺ concentration at interface of sulphonic acid and carboxylic layers on current efficiency: 3–4 N NaCl; 1.0–5.5 kA m⁻²; 33% NaOH.

In summary, the results indicate that the Na⁺ concentration at the interface between the sulphonic and carboxylic layers in the normal membrane is substantially depressed from that of the anolyte compartment, and that the concentration at this interface strongly affects the current density.

17.3.2 Investigation of limiting current density

The limiting current density may be defined as the current density at which the depression of the Na⁺ concentration at the interface of the membrane's sulphonic and carboxylic layers results in an abrupt rise in cell voltage and drop in current efficiency.

A small, high-circulation laboratory cell was used to investigate this phenomenon and the relationship between current density, cell voltage, and current efficiency, with the Aciplex F-4401 membrane and with a membrane that currently provides high performance in widespread commercial use at approximately 4 kA m⁻². With the electrolyte circulation in the cell raised to a level corresponding to more than 300 times that normally applied in a large-scale electrolyser, in order to prevent the formation of a Na⁺ diffusion layer at the membrane surface and, in this sense, to virtually eliminate the influence of changes in the relative rate of Na⁺ diffusion into the membrane, the results shown in Fig. 17.8 were obtained. With the F-4401 and a brine concentration of 3.5 N NaCl, the current efficiency showed little or no decline at up to 10 kA m⁻² and only a moderate decline at up to the maximum tested current density of 18 kA m⁻², with no sign of any limiting current density throughout the test range. In contrast, with the other membrane and a brine concentration of 2.5 N NaCl, the current efficiency declined sharply at 6 kA m⁻² and above.

The results indicate that ultra-high current densities of up to 10 kA m⁻² or more should be feasible in large-scale electrolyzers, if a high level of electrolyte mixing and concentration uniformity can be maintained in the cell compartments and a high ion

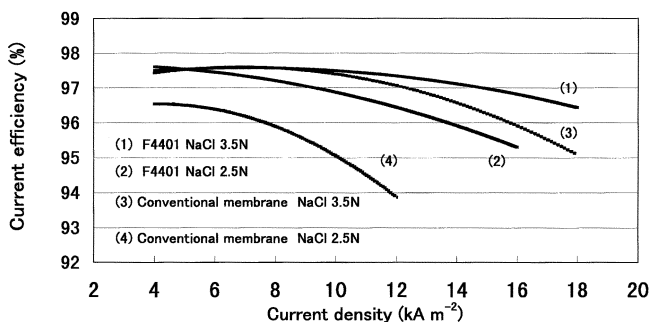


Fig. 17.8 Current efficiency at high current densities in a high-circulation laboratory cell: 32% NaOH; 90°C.

concentration can be maintained at the interface of the sulphonic and carboxylic layers.

17.3.3 Maintenance of flow in a large electrolyser

The circulation conditions obtained in the small laboratory cell cannot be attained in a full-scale cell. The effects of Na^+ diffusion to the membrane and non-uniformity in its intracell concentration cannot be entirely eliminated, and a greater decrease in current efficiency will tend to occur at high current densities.

In a large-scale electrolyser, if no provision is made to promote the internal circulation, a gas bubble zone tends to form in the upper part of the anolyte compartment as shown in Fig. 17.9. As shown in Figs 17.10 and 17.11, this tendency increases at high current densities, and in some cases the gas bubbles may comprise nearly 90% of the space and cause a corresponding decline in brine concentration. Throughout this zone, fluid movement is extremely slow and the diffusion of ions to the membrane is therefore quite limited. To prevent this effect and maintain a high current efficiency at high current densities, it is therefore essential to design the electrolyser for optimal flow of both gas and liquid, particularly in the upper region of the anolyte compartment.

17.4 Requirements for operation at high current density

17.4.1 Ion-exchange membrane

Because the Na^+ transport number is generally higher in the carboxylic layer than in the sulphonic layer and tends to result in low Na^+ concentrations at the interface between these two layers, the maintenance of a sufficiently high concentration in this region under high current density requires that the sulphonic layer itself exhibits firstly, a high rate of brine diffusion and second, a high Na^+ transport number. The Aciplex F-4401 has been developed to meet both requirements, by optimisation of the thickness and ion-exchange capacity of both the sulphonic and the carboxylic layers,

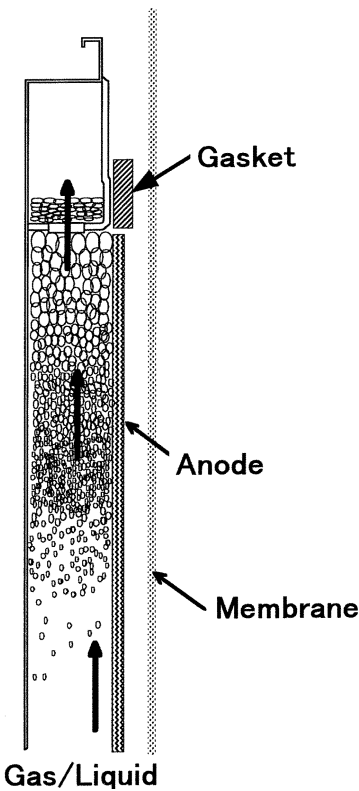


Fig. 17.9 Conformation of gas bubble zone in anolyte compartment.

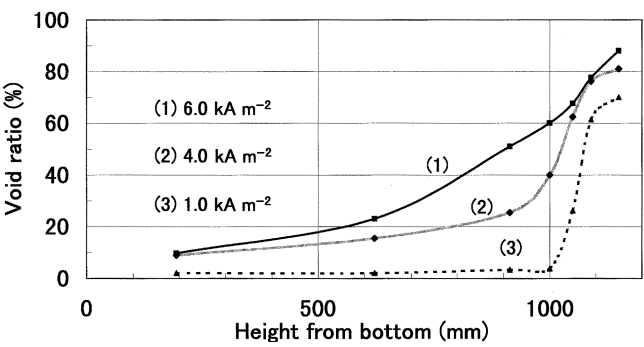


Fig. 17.10 Gas bubble distribution in anolyte compartment of commercialised electrolyser without baffle: 3.5 N NaCl; 40 kPa; 90°C.

and by use of sacrificial threads in the membrane reinforcement. The result is stable, efficient electrolysis at current densities higher than those attained with previous ion-exchange membranes.

17.4.2 Electrolyser

For high current efficiency at high current densities, it is essential that the electrolyser provides efficient mass transfer to the membrane surface. The most important

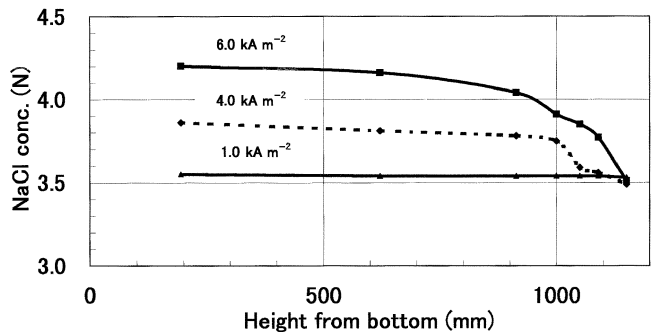


Fig. 17.11 Vertical NaCl distribution in anolyte compartment of commercial electrolyser without baffle: 3.5 N NaCl; 40 kPa; 90°C.

requirements for the electrolyser are therefore the maintenance of fluidity in the upper part of the anolyte compartment and a uniform distribution of anolyte distribution throughout that compartment.

At high current densities it is also particularly important to ensure that the electrolyser is free from pressure-induced vibrations, which may quickly lead to membrane damage. The vibrations tend to arise if waves form in the gas-bearing liquid in the electrolyser's gas-liquid separation chamber and block the egress of gas through the nozzle of the chamber outlet, as illustrated in Fig. 17.12, leading to sharply fluctuating pressure in the chamber.

The ML32NCH high current density electrolyser was specifically designed and developed to meet all of these requirements.

17.5 The ML32NCH electrolyser

Key characteristics of the ML32NCH electrolyser for operation at high current densities, shown schematically in Fig. 17.13, are given in the subsections below.

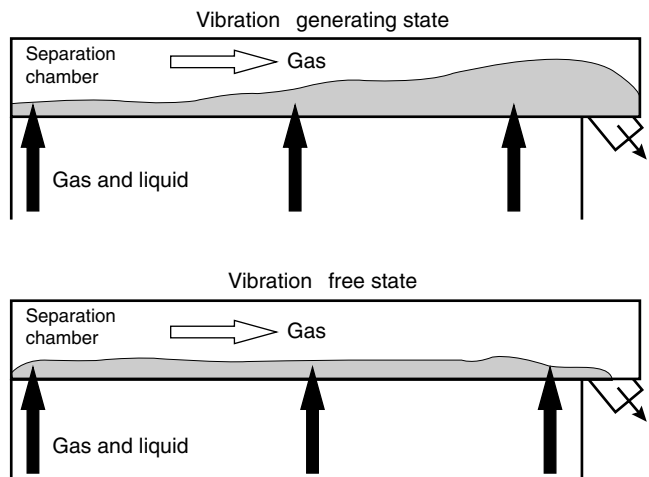


Fig. 17.12 The mechanism of vibration generation in the gas-liquid separation chamber.

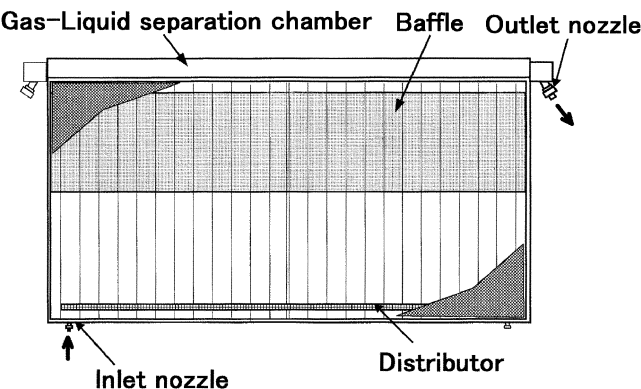


Fig. 17.13 Cell structure of the new ML32NCH electrolyser.

17.5.1 Anolyte compartment baffle

The baffle in the anolyte compartment ensures effective mixing in the upper part of the compartment (where gas bubbles tend to collect) and a sufficient supply of ions to the membrane in that region. The baffle ensures a highly uniform anolyte concentration throughout this region, and also promotes its uniformity throughout the entire anolyte compartment.

17.5.2 Brine distributor

The brine distributor provides a uniform supply of anolyte throughout the bottom region of the anolyte compartment. In conjunction with the baffle in the upper half of the compartment, this results in a highly uniform concentration throughout the anolyte compartment, as shown in Fig. 17.14, by the measured values obtained during operation of the electrolyser at a current density of 6 kA m^{-2} .

17.5.3 Separation chamber

The gas-liquid separation chamber has been redesigned and a gas-permeable porous plate has been incorporated to prevent the formation of waves in the liquid. These

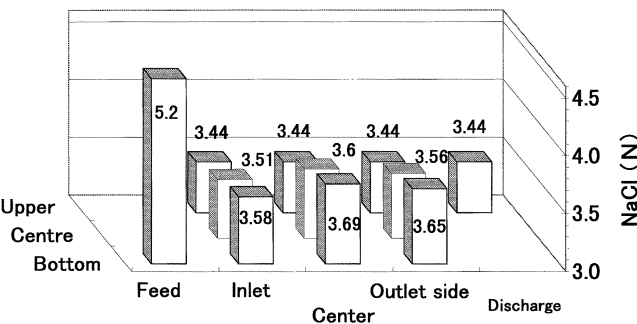


Fig. 17.14 NaCl concentration in the anolyte compartment of the ML32NCH cell operating at 6 kA m^{-2} , 32% NaOH and 90°C .

would block the egress of gas from the chamber and induce strong pressure fluctuations, even with the generation of large volumes of gas and liquid high in gas content, which obtains under operation at 6 kA m^{-2} and higher. As indicated in Fig. 17.15, the chamber is completely free from any significant pressure fluctuation in the high current density range.

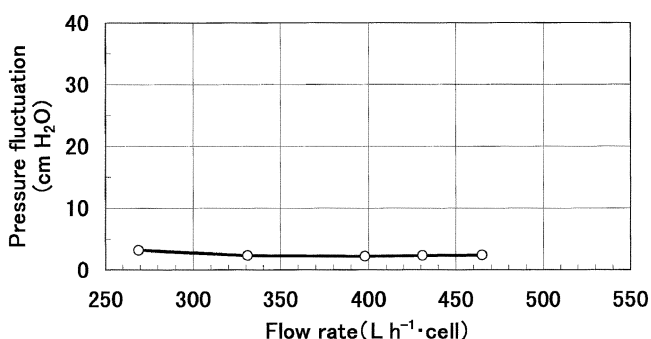


Fig. 17.15 Pressure fluctuation in the anolyte compartment of the ML32NCH cell operating at 6 kA m^{-2} , 32% NaOH and 90°C .

17.6 Performance in commercial operation

The ML32NCH electrolyser equipped with the Aciplex F-4401 membrane has been in commercial operation at 6 kA m^{-2} for approximately one year at Asahi Chemical's chlor-alkali plant. As shown in Figs 17.16 and 17.17, the electrolyser has achieved a cell voltage of 3.17 V and a current efficiency of 96%, while operating at 6 kA m^{-2} . This operation is continuing; the present plan is to investigate the performance of the ML32NCH at a current density of 8 kA m^{-2} .

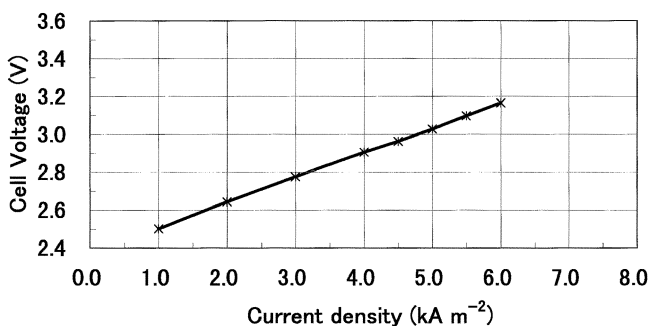


Fig. 17.16 The relationship between current density and cell voltage in the ML32NCH electrolyser with the F4401 membrane: 3.5 N NaCl; 32% NaOH; 90°C .

A zero-gap electrolyser is currently under trial. In pilot-scale operation, it has demonstrated a cell voltage of 3.0–3.1 V at a current density of 6 kA m^{-2} . The results indicate that completion of zero-gap technology will bring a further reduction in unit power consumption of 100 kWh per tonne of NaOH.

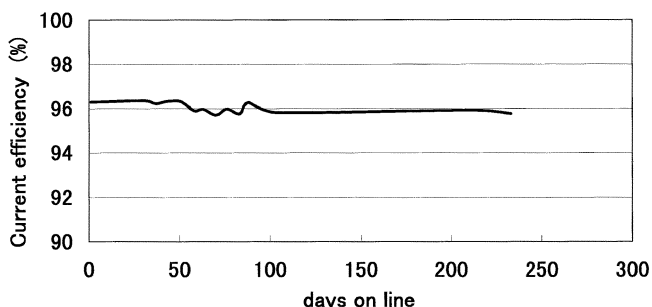


Fig. 17.17 Performance of the ML32NCH electrolyser with an F4401 membrane in a commercial operation at 6 kA m^{-2} , 3.5 N NaCl, 32% NaOH and 90°C .

17.7 Continuing effort

The development of high current density electrolysis technology is a continuing effort. Asahi Chemical's focus is currently on the confirmation of stable long-term performance and reliability, in preparation for the supply of this process equipment and technology to chlor-alkali producers.

Many other goals lie ahead for the further advancement of the membrane chlor-alkali process and technology. Asahi is dedicated to achieving these goals and to providing new standards of efficiency and performance in the future.

Chapter 18

Chlor-Alkali Membrane Electrolyser

S Collings

18.1 Introduction

ICI has been involved in the production of chlorine for over a hundred years. During that time different technologies have been used to produce chlorine, including mercury, diaphragm and membrane technologies. The technologies used have been developed by ICI using the company's research and development capabilities. Today ICI has an installed chlorine capacity in excess of one million metric tonnes per annum.

In 1981 ICI created a business to license membrane technology to chlor-alkali producers around the world calling that business ETB (Electrochemical Technology Business). ICI ETB has licensed over 40 plants around the world during that time mainly using its FM21TM monopolar technology. FM21TM, and more recently FM1500 have proven to be the right choice of technology for some types of producers in the market. The FM1500 is the first choice for expansions, conversions, hypo plants, smaller new plants and pulp and paper applications.

Several years ago, ICI ETB looked at the total market for chlor-alkali membrane technology and considered how to develop an electrolyser that would extend its product and market range. A detailed analysis was carried out and many chlor-alkali producers were consulted. As a result of this work ICI ETB has developed an electrolyser called BiChlor.

Set out in the sections below are the stages that ICI ETB went through in developing BiChlor. Some of the features of BiChlor are also discussed and finally the performance of the technology is displayed.

18.2 Stage 1: setting the standards

18.2.1 Market requirements

ICI ETB identified that in order to ensure that it has the technology to provide solutions across the full range of the market, a world-scale bipolar electrolyser was needed in addition to the proven and excellent FM1500.

World-scale producers use spreadsheet analysis to evaluate the economics of different options over the lifetime of the plant (often 20 years is assumed), taking account of operating, maintenance and capital costs. The chlor-alkali industry also expects the current density (CD) to increase in a manner that is dependent on membrane development. Other important factors expressed by producers about membrane technology choice included component lifetimes and reliability.

18.2.2 The benchmark

ICI ETB attempted to define an 'industry norm' for electrolyzers in order to ascertain the effect of changing different parameters. Determination of the industry norms for electrolyzers in 1999 provided the following:

- current density: 5 kA m^{-2}
- power consumption: less than 2200 kWh per metric tonne of 100% NaOH
- membrane lifetime: 3 years
- rate of voltage rise: 10 mV per month
- rate of current efficiency decline: maximum of 0.5% per year.

These performance norms were analysed along with typical cash spend profiles. An example of spending by area on electrolyzers is given in Fig. 18.1. ICI ETB discounted these figures to give a net present cost and then analysed which factors had the biggest effect. One factor that was extremely dominant in this analysis was power price.

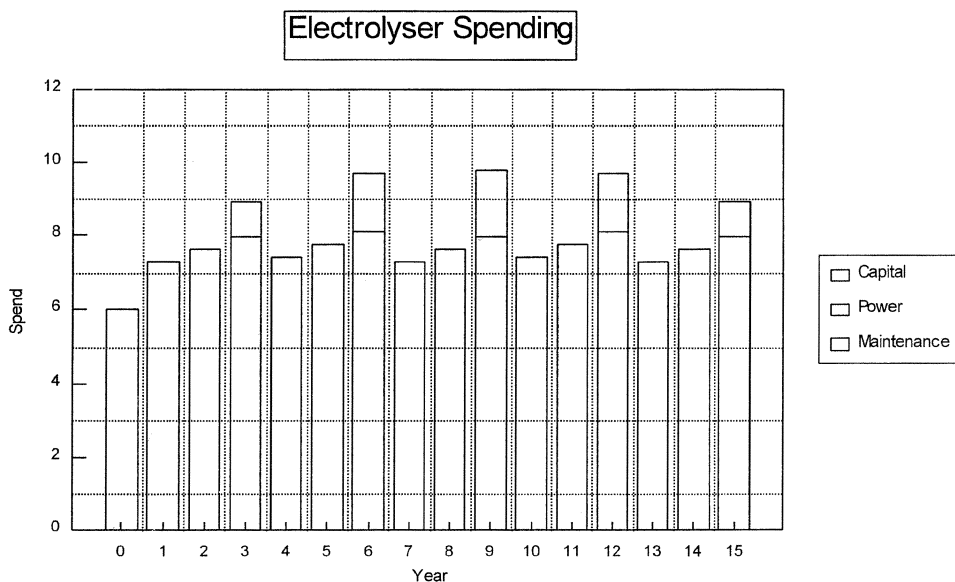


Fig. 18.1 Typical spending on an electrolyser by cost area.

However, the learning seemed to be the same for different power prices with the magnitude becoming more or less pronounced. The findings set out below represent a medium power price and a normal discount rate for Europe:

- decrease initial power consumption by 100 kWh per tonne: -3.5%
- halve the rate of voltage rise: -3.6%
- halve the rate of CE decline: -0.4%
- increase membrane lifetime by 1 year: -0.3%
- achieve all of the above: -9.4% .

A further analysis was performed to look at the optimum current density. This was completed using ICI ETB's base-case data for different power prices. Analysis of the electrolyser incorporating all of the improvements (listed above) was also undertaken and the results are shown in Fig. 18.2.

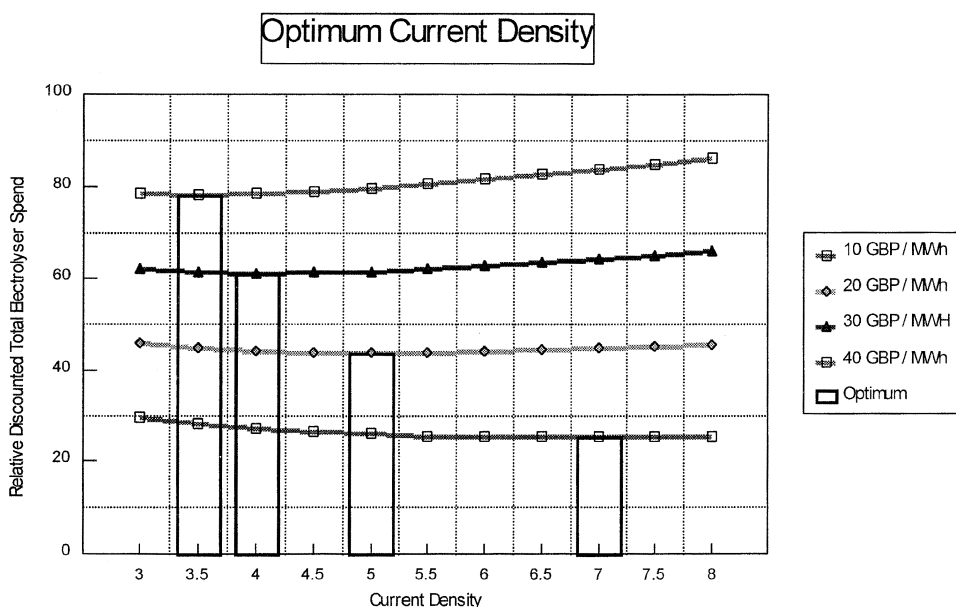


Fig. 18.2 Comparison of optimum current densities for different operating power prices.

The optimum current densities were fairly similar for the base-case and the 'improved' electrolyser. These data were surprising as they suggest that there is little incentive to acquire CDs higher than 5 kA m^{-2} unless the power price is low. It should be noted though that these lines are flat across a range of current densities suggesting that, within reason, choice of current density is not critical over the lifetime of a chlorine plant as savings in capital are balanced by increases in power consumption. There seems little incentive in going for high CDs, which

represent an increased risk of failure unless there are very tight restrictions on available capital.

18.2.3 Overall targets for BiChlor

ICI ETB decided that its new technology would be a bipolar electrolyser. Bipolar allows a larger unit size of electrolyser without incurring voltage penalties and, for larger sized plants, provides cost savings in other parts of the cellroom (e.g. bus bars). Moreover it was a technology the market wanted!

The membrane area was chosen to give the optimum combination of economies of scale, ease of handling, and use of available raw material and membrane sizes. This led us to a membrane cross sectional area of approximately 3 m^2 .

Given the analysis described in Section 18.2.2, it was decided to develop an electrolyser that was capable of running comfortably at 6 kA m^{-2} . To ensure this requirement, BiChlor is designed for 8 kA m^{-2} . This provides the flexibility to use BiChlor at very high current densities to suit the needs of particular clients and allows for advances in membranes which might move the optimum current density upwards.

Finally, an electrolyser which has low voltage at start-up and very stable operation during its lifetime was designed. Advantages of these features are longer component lifetimes and reliable operation.

18.2.4 Modular or filter press?

There are two principal ways in which an electrolyser can be constructed.

A filter-press electrolyser allows the back of a cathode to be welded to the back of the next anode. This does not, unfortunately, lend itself easily to sealing the gaskets using bolts but more commonly requires a closing pressure to be applied to all of the gaskets. This design also typically requires the pack to be split at the position of a membrane that makes fitting of membranes a more difficult and time-consuming procedure, which has to be done *in situ*, often in an operating cellroom where increased care is required to avoid safety risks and downtime.

A modular electrolyser contains a number of discreet modules consisting of anode, membrane and cathode. These sealed modules can be individually removed from the electrolyser without the other modules being affected. The key to this type of design is to ensure a good electrical contact between adjacent modules.

BiChlor is modular in design and the name ‘Nestpak’ was termed for one module. This design provides increased operability and good pack sealing (essential for reliable operation). The Nestpak design also allows for maintenance work (such as the changing of membranes) to be performed in the workshop rather than in the cellroom. Perhaps most significantly, the Nestpak design keeps downtime to an absolute minimum – an important factor on a production-limited plant.

Figure 18.3 illustrates how a BiChlor Nestpak can be removed from and returned to the electrolyser.

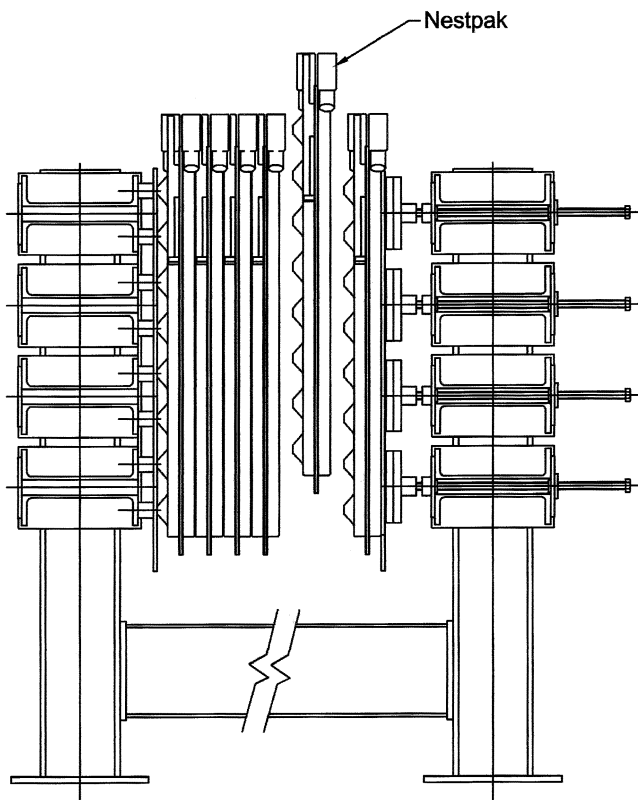


Fig. 18.3 Schematic of the removal of a Nestpak from a BiChlor electrolyser.

18.3 Stage 2: BiChlor – performance by design

18.3.1 Achieving stable voltage and current efficiency

The analysis of ICI ETB (described in Section 18.2) showed that stable voltage was the dominant factor to be considered. The many years of experience that ICI has in designing, operating and providing technical support for chlor-alkali plant has provided the knowledge that stable voltage (and current efficiency) is achieved by:

- good brine quality
- good control of operating parameters
- keeping shutdowns and load swings to a minimum
- using robust/stable membranes
- having robust/stable electrode coatings
- ensuring that the membranes are never subjected to a high degree of gas voidage and are fully flooded
- having an even concentration of electrolytes within the electrolyser
- having even current distribution to the electrodes.

Of the factors just listed, those that critically influence the design of the electrolyser are described below.

18.3.2 Minimising gas voidage by design

It is well known to most membrane technology operators that if a membrane sees a lot of gas for most of the time, rather than liquid, that this leads to deterioration of the membrane such as blistering, drying out and ultimately to failure. Membranes operating with gas at the top of the electrode are not operating at optimum conditions and this leads to an increase in voltage owing to an increasing proportion of gas rather than liquid. It also leads to a current density increase in the flooded membrane area. To prevent a high degree of voidage at the top of the electrode several design features can be incorporated into the electrode. A limit is set on the height of the compartment, thus limiting the build-up of gas bubbles as they rise through the compartment.

To remove gas from an electrolyser compartment the obvious choice is to take it out at the top. In addition, it is important that the gas can leave the compartment along its entire length in order to avoid any back pressure. This is exactly the way BiChlor is designed, which is illustrated in Fig. 18.4.

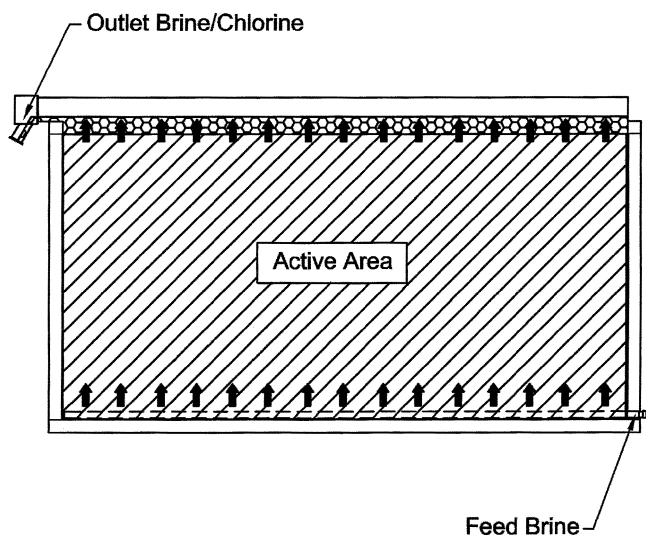


Fig. 18.4 Outlet header and gas/liquid escape.

In order to ensure that the liquor level in the BiChlor is always higher than the top of the membrane and the membrane is fully flooded during operation, the gas exit header also acts as the liquor outlet header. Liquors overflow from the outlet header of each compartment as shown in Fig. 18.4.

18.3.3 Uniform concentration of electrolytes over the surface of the electrode by design

In BiChlor this feature is achieved by:

- (1) even distribution of electrolyte feed across the base of each compartment;
- (2) uniform removal of electrolytes vertically across the top of each compartment (as described above); and
- (3) providing a high degree of vertical mixing within each compartment.

The uniform distribution of feed liquor is achieved by the use of a specially engineered distribution pipeline running internally along the base of each compartment and containing a number of carefully designed apertures along its length.

The vertical mixing is enhanced using a baffle system. This uses the gas lift principle on the front face to increase upward liquor flow. A corresponding downward flow of gas-free liquor is drawn down the back face of the baffle thus creating an increased vertical circulation. Measurements at the test facilities of ICI ETB have demonstrated a recirculation flow ratio of recirculated flow to inlet flow of approximately 70 : 1, depending on the operating current density.

18.3.4 Uniform current distribution by design

BiChlor contains mesh electrodes, the design of which has been carefully selected to have the most beneficial combination of gas and liquor transport, membrane support and high current-carrying capability.

Current is transferred to these meshes using distributors called 'spiders'. The spiders have legs which distribute current to the mesh. The location of the spiders and the distribution of the anode and cathode spider legs has been developed via extensive calculation and trial to minimise the resistance of the spider/membrane/mesh combination and to ensure that the resistance to current flow is equal across the whole membrane area, thus ensuring that there are no localised non-uniform current paths. The spiders are shown in Fig. 18.5 and the distribution pattern is shown in Fig. 18.6.

18.3.5 Achieving a low power consumption

Low power consumption is obtained by:

- using optimum operating conditions
- choosing high-performance membranes
- using low-voltage electrode coatings
- minimising resistances within the electrolyser

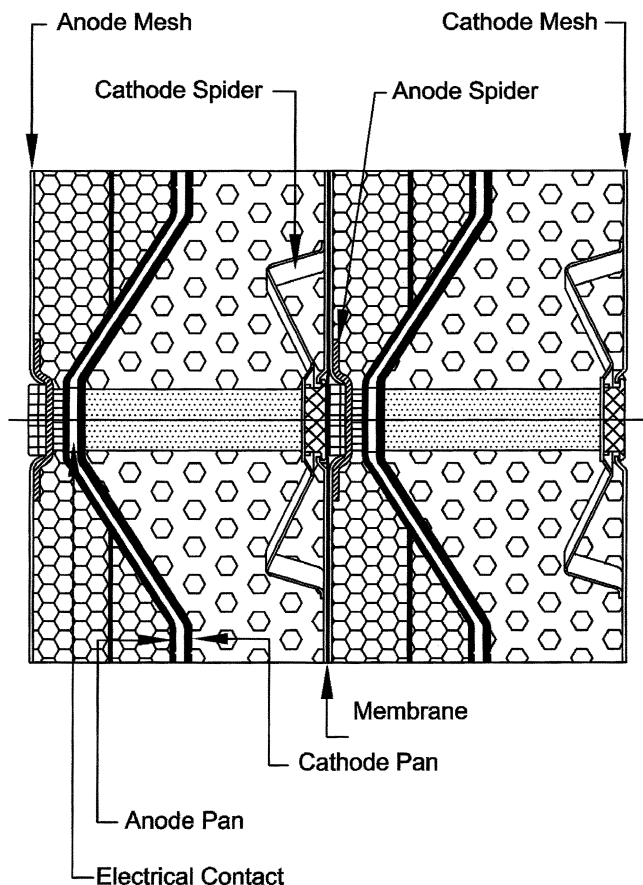


Fig. 18.5 Specialised BiChlor mesh electrode design incorporating 'spider' current distributors.

- ensuring that the membranes are fully flooded
- having a uniform concentration of electrolytes
- ensuring a uniform current distribution across the membrane
- an optimised electrode design to give low voltage drop coupled with good bubble release
- achieving a very low resistance between Nestpaks

18.3.6 Low electrical resistance paths by design

BiChlor contains a number of features to lower the electrolyser voltage by reducing the resistance. One of these features is the design for zero gap operation. This lowers the electrolyser resistance by keeping the distance from the electrodes to the membrane at a minimum.

Another feature that minimises resistance is the choice of electrode mesh. ICI ETB carried out extensive trials of different electrode designs including different types of mesh. The designs were computer-modelled and tested to find the optimum combi-

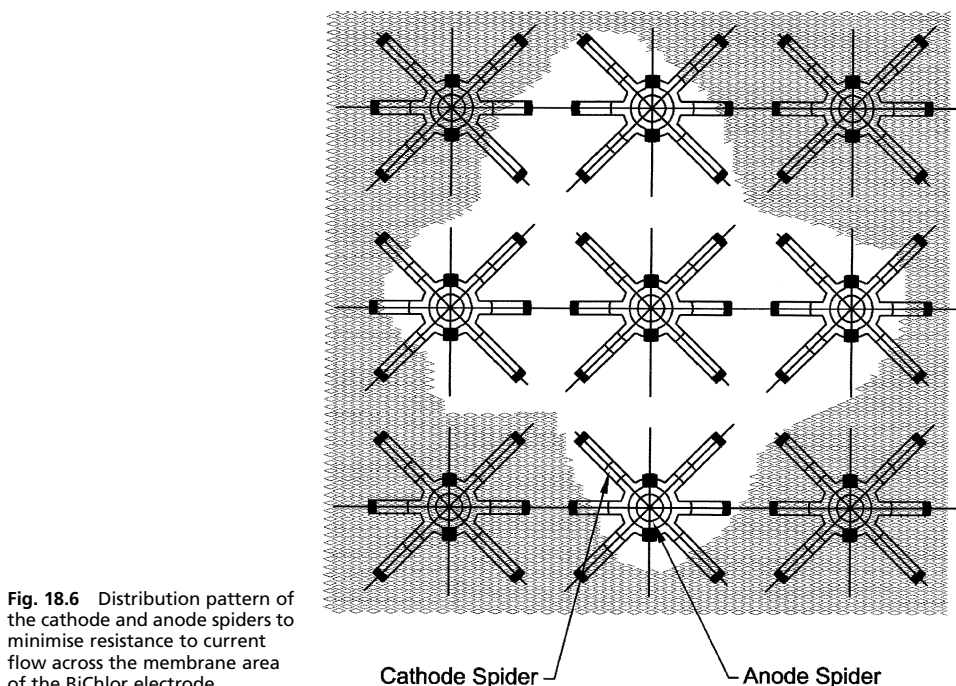


Fig. 18.6 Distribution pattern of the cathode and anode spiders to minimise resistance to current flow across the membrane area of the BiChlor electrode.

nation of current-carrying capability, largest surface area for electrolysis and ease of bubble release.

This leads on to an explanation of the reason for each BiChlor Nestpak containing a number of 'dimples'. These dimples can be seen in the cut-away drawing of a BiChlor electrolyser (Fig. 18.7). The circular dimples on the cathode side point outwards and on the anode side point inwards. These dimples fit into one another when the Nestpaks of BiChlor are pushed together.

The dimples enable the maximum use of nickel (a good conductor of electricity) and the minimum use of titanium (a poor conductor of electricity). This is most easily seen by referring to Fig 18.5. The arrangement reduces appreciably the resistance of the current path between the cathode and the anode of adjacent modules.

18.3.7 Achieving longer membrane lifetimes

The lengthening of membrane lifetimes is achieved by:

- good brine quality
- good control of operating parameters
- good control of shutdowns and load changes
- use of robust membranes
- ensuring that the membranes are fully flooded

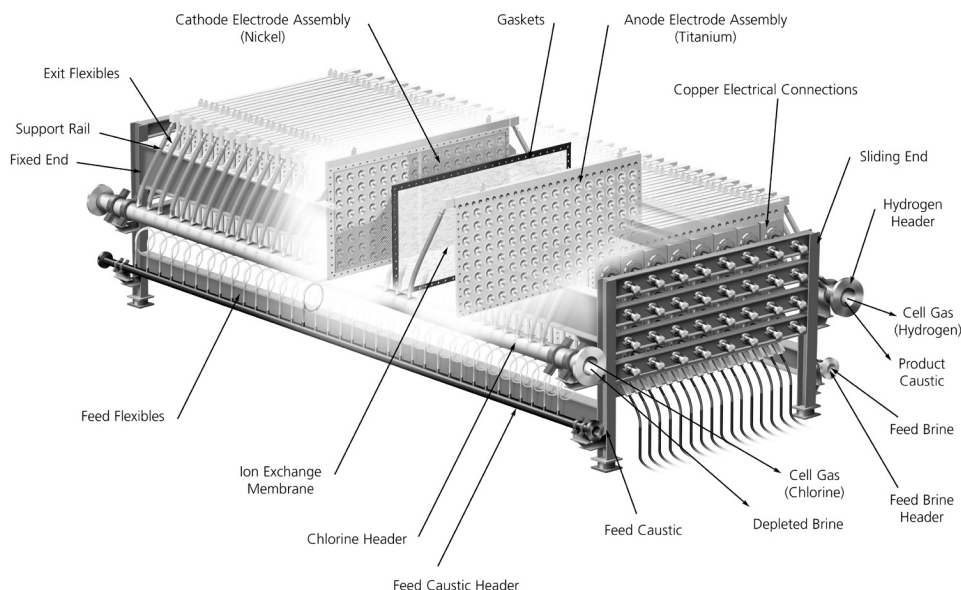


Fig. 18.7 Cut-away of the BiChlor electrolyser.

- having an even concentration distribution of electrolytes within the electrolyser
- having a uniform current distribution across the electrodes
- providing a sealing system that will last for longer than the membranes

It can be seen that most of the points listed above are consistent with achieving stable operation. One new point is described below.

18.3.8 Advanced sealing by design

Each Nestpak module in the BiChlor electrolyser is sealed along its perimeter by a combination of a bolted flange and gaskets. This allows the sealing pressure to be controlled around all of the perimeter of each individual Nestpak. In a large-area bipolar filter-press electrolyser, sealing is only achieved with massive compression equipment and even then a variable sealing pressure is likely to exist around the module perimeter.

The gaskets in BiChlor have been very carefully designed to provide a high sealing pressure with minimal gasket stress. Selection of gasket material has also been achieved ensuring the right combination of properties. The gasket design has taken account of ICI ETB's extensive design and materials selection experience proven in the FM21TM where gasket lifetimes are in excess of 5 years.

18.4 Stage 3: the performance

18.4.1 BiChlor delivers

After conducting trials on various prototypes and testing a large number of components over many years, ICI ETB installed a BiChlor demonstration electrolyser at ICI's Lostock Plant in the UK. The BiChlor electrolyser achieved an oxygen content of approximately 1.5% in chlorine with alkaline feed brine.

The electrolyser has been operated over a range of current densities. Figure 18.8 shows the performance of the electrolyser normalised to an operational current density of 5 kA m^{-2} (the data are broken down in Table 18.1). Furthermore, ICI ETB's operating personnel confirm that one Nestpak can be changed in less than 4 h (power off to power back on).

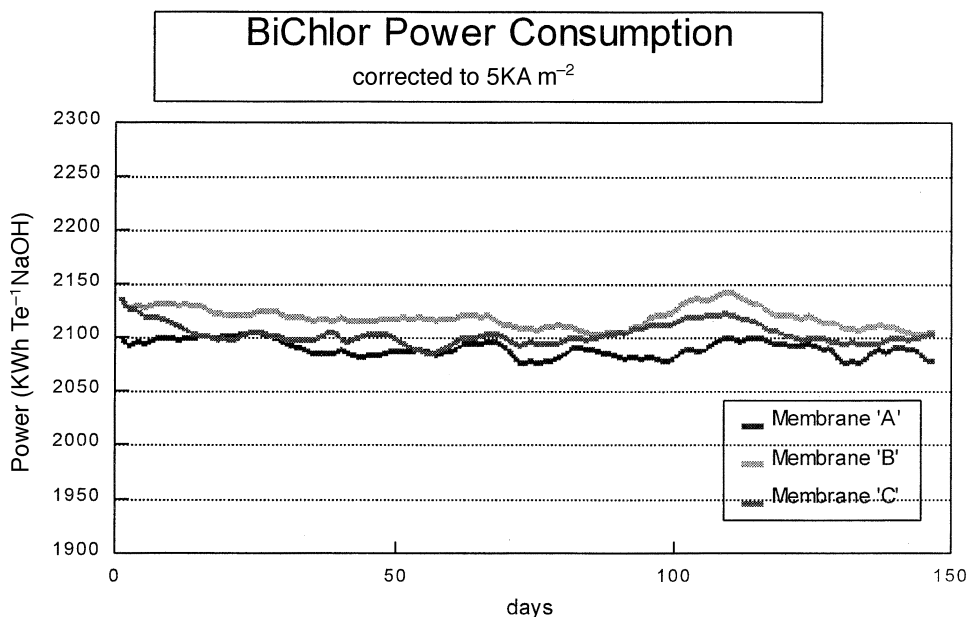


Fig. 18.8 Plot of power consumption of the BiChlor electrolyser for different membranes. Data breakdown is given in Table 18.1.

Table 18.1 Typical performance data of the BiChlor electrolyser operating at 5 kA m^{-2} (taken from Fig. 18.8).

Property	Membrane A	Membrane B	Membrane C
Voltage	3.02	3.05	3.02
Current efficiency	97.0%	96.0%	96.0%
Power (kWh per tonne of NaOH)	2086	2129	2108

18.5 Summary

- BiChlor is the new bipolar membrane electrolyser from ICI ETB
- FM1500 is ICI ETB's advanced monopolar electrolyser which is excellent for some types of project
- With FM1500 and BiChlor, ICI ETB has the technology to suit all project needs
- BiChlor is the result of extensive market research and operating experience
- BiChlor contains a unique combination of features which offer considerable benefits to the chlor-alkali producer
- BiChlor delivers *Lowest Lifetime Costs By Design*

Chapter 19

Advanced Cell Technology with Flemion® Membranes and the AZEC® Bipolar Electrolyser

T Shimohira, T Kimura, T Uchibori and H Takeda

19.1 Introduction

Asahi Glass Co., Ltd (AGC) is one of the largest chlor-alkali producers in Japan. The company's total domestic capacity of caustic soda including its affiliates' is greater than 1 000 000 metric tonnes per year. AGC has extended its production capacity to Southeast Asia to ensure more than 500 000 metric tonnes per year as its affiliates' capacity. AGC's technology and know-how on AZEC® electrolyzers and Flemion® membranes originates from operation experiences in its own chlor-alkali plants. Several types of AZEC® electrolyzers have been developed based on this experience and have been adopted by more than 60 end-users around the world with a total capacity of some 4 400 000 metric tonnes of caustic soda per year. Flemion continues to be one of the most popular membranes for more than 100 'ion-exchange membrane' process users. AGC is convinced that it is in a good position to feedback user demands and to exploit its own experience to guide the development and improvement of its electrolyser and membrane technology.

AGC has been recently focusing on the development of a new electrolyser and a new membrane for high current density operation, a facility much requested by many users. In July 1998, AGC completed the conversion of its last diaphragm process plant to the then newest Bipolar Electrolyser, the AZEC® B-1 (hereinafter, B-1) with Flemion® F-893 (hereinafter, F-893) membrane and also the then-newest membrane Flemion® Fx-8964 (hereinafter, Fx-8964). This conversion was the result of AGC's development efforts. AGC is now on the way to the next stage of its ion-exchange membrane technology, where 6 kA/m^{-2} operation will be the norm and 8 kA/m^{-2} operation will be made a feasibility.

This chapter outlines the development of the above process.

19.2 The recent general outlook of AZEC® B-1, the efficient bipolar electrolyser

B-1 has already been licensed to eight chlorine producers since 1997. The total capacity of these B-1 plants has exceeded 440 000 metric tonnes per year (caustic

base). The B-1 plant located at AGC's Kashima factory has a capacity of 200 000 metric tonnes per year and has been operated under the remarkable condition of maximum current density of 5.7 kA m^{-2} since July 1998. The plant came into operation successfully and has been operated stably since 1998 (demonstrated by the plot shown in Fig. 19.1). A total of 18 B-1 electrolyzers have been sited in Kashima. At the facility, the F-893 membrane has been installed in 16 electrolyzers and the Fx-8964 experimental membrane for high current density work has, as of 1998, been installed in two electrolyzers. The total capacity of all B-1 plants is now 640 000 metric tonnes per year.

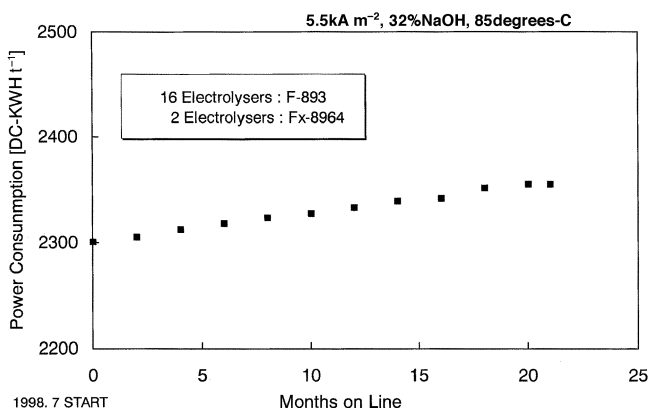


Fig. 19.1 Performance plot of the AZEC® B-1 electrolyser at the Kashima factory operating at 5.5 kA m^{-2} .

19.3 AZEC® Improved B-1: the high performance bipolar electrolyser for high current density operation

The lower running cost and the higher current density operation – thereby reducing the investment capital – are the eternal requests of all chlorine producers around the world. AGC has improved the inner structure of the original B-1 electrolyser extending its practical current density up to a value of 6 kA m^{-2} while at the same time reducing the cell voltage. The AZEC® Improved B-1 (hereafter, Improved B-1) can attain a lower cell voltage at 6 kA m^{-2} than that of the original B-1 at 5 kA m^{-2} . The Improved B-1 has already been put on the market and licensed to two chlorine producers. The total capacity of these plants is approximately 90 000 metric tonnes of caustic soda per year. Practical 6 kA m^{-2} operation has been finally assured by the stable performance during a test run using a commercial-scale cell with the Fx-8964 membrane at 7 kA m^{-2} . AGC intends that the Improved B-1 can be operated under higher current densities of up to 8 kA m^{-2} , from both the hydraulic and electrical viewpoints.

The Improved B-1 has utilised both the fundamental technology and the structure of the B-1 electrolyser together with newer and enhanced technology, all of which is necessary for the stable operation of the unit at high current density. Four important items are detailed below:

- (1) Gas lift circulation of the electrolyte inside each chamber is enhanced from B-1.
- (2) 'DAM'-type overflow for discharging gas and liquid from each chamber as is found in the B-1 system.
- (3) 'M'-shape rib, which works as a downcomer, an electrical conductor and a structural support (enhanced from B-1).
- (4) Bipolar plate connecting the anode pan and the cathode pan (as in B-1).

AGC has developed a new cell structure to reduce the gap between the anode and cathode without damaging the membrane in the Improved B-1.

19.3.1 Advantages of the AZEC® Improved B-1

The above-mentioned technology and structure provide advantages for the Improved B-1 electrolyser in performance and reliability even under high current density. Good electrolyte distribution and no gas stagnation in each chamber, smooth discharge of gas and liquid, and low ohmic drop are necessary to overcome the difficulties of high current density operation.

Good electrolyte distribution

Needless to say, uniform concentration distribution of an electrolyte over a membrane surface is the most important factor to maintain good membrane performance. Sufficient internal circulation results in good electrolyte mixing inside the chamber. As shown in Fig. 19.2, 12 ribs installed in both anode and cathode chambers work as downcomers in the same manner as in B-1. The horizontal cross-sectional area of the downcomer in the Improved B-1 has been approximately doubled. All electrolyte concentrations measured at various points over the whole electrolysis area are maintained at specification, even at 6 kA m^{-2} through to 8 kA m^{-2} , as is shown in Fig. 19.3 (with the relevant data at the downcomer positions 1–4 given in Table 19.1).

Smooth discharge of gas and liquid

The DAM-type overflow, as shown in Fig. 19.4, has been applied to the Improved B-1 for discharging gas and liquid. It is very effective—even under higher current density—in the smooth discharge of gas and liquid.

Gas and liquid flow up along the membrane, then turn to the inlet of a narrow channel at the top of the chamber. This flow pattern enhances continuous replacement of electrolyte over the whole membrane surface. It is especially effective in eliminating gas stagnation at the top zone of the electrolysis area. The DAM-type system ensures that the fine-bubble flow is constant through its narrow channel and that smooth gas separation occurs at the outlet of the channel. Gas and liquid flow separately through an upper duct, an outlet nozzle and an outlet hose, then to a

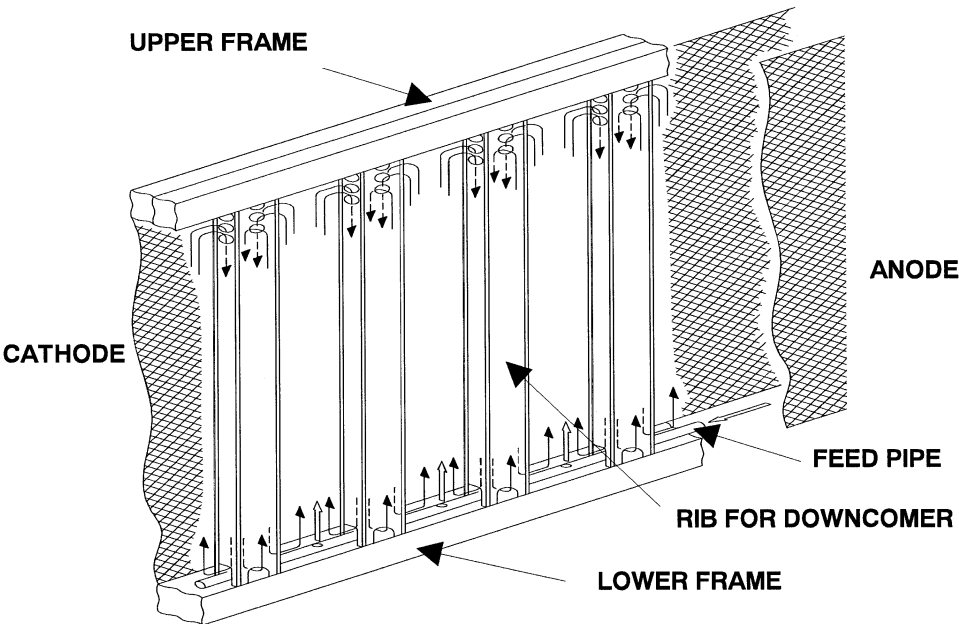


Fig. 19.2 Internal electrolyte circulation (AZEC® Improved B-1 electrolyser).

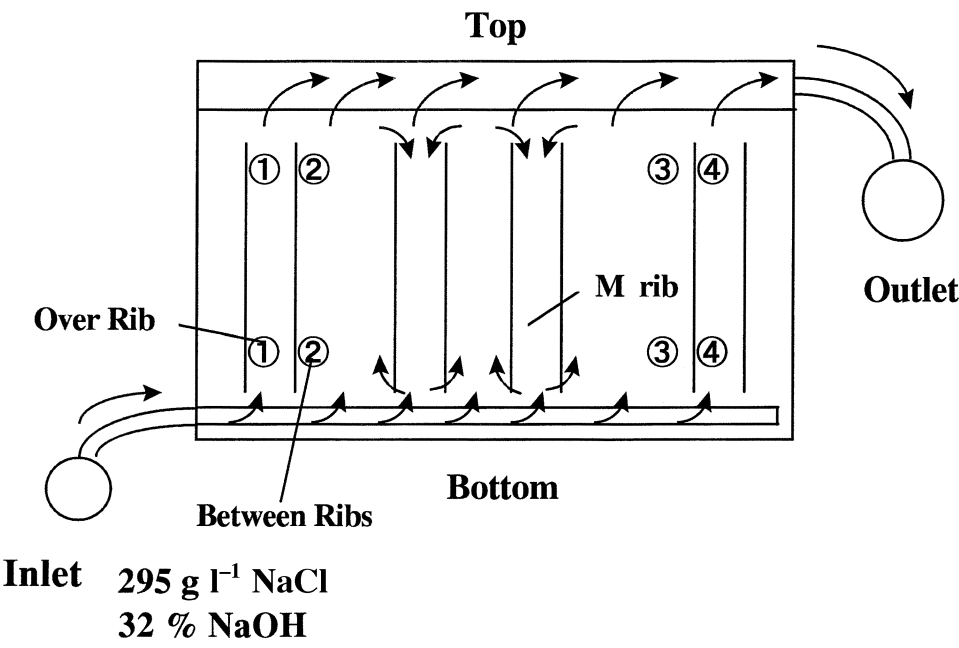
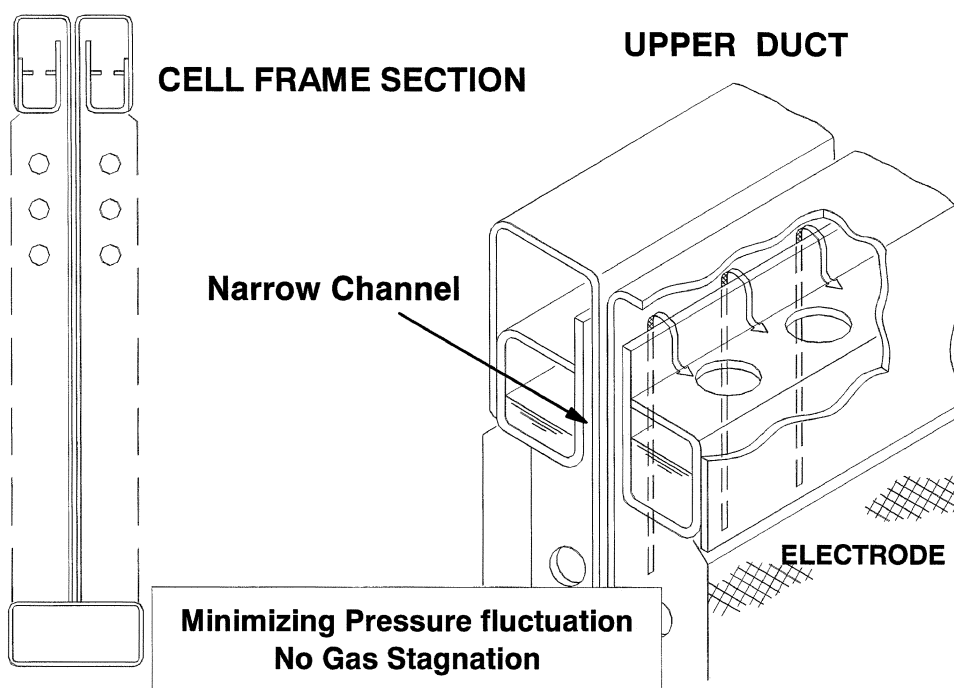


Fig. 19.3 Electrolyte distribution in a full-scale pilot cell of the AZEC® B-1 electrolyser. Statistical breakdown is provided in Table 19.1.

Table 19.1 Data to be read in conjunction with the electrolyte distribution at positions 1–4 in Fig. 19.3.

Electrolyte	Location	Position			
		1	2	3	4
At 6 kA m ⁻² NaCl (g l ⁻¹)	Top	194.0	196.0	196.0	195.0
	Bottom	211.0	218.0	213.0	207.0
	Top	32.3	32.4	32.5	32.3
	Bottom	32.0	32.1	32.1	32.1
At 8 kA m ⁻² NaCl (g l ⁻¹)	Top	198.0	194.0	193.0	194.0
	Bottom	215.0	220.0	216.0	210.0
	Top	32.4	32.4	32.4	32.2
	Bottom	32.1	32.0	32.0	32.0

**Fig. 19.4** Dam-type system of the AZEC® B-1 and Improved B-1 electrolyzers.

header, as shown in Fig. 19.5. In this design, the membrane is free from the salt blistering effects arising from chlorine gas stagnation and from the abrasion problems due to pressure fluctuation, even under high current density. Neither gas stagnation nor abrasion has been found on inspecting the membrane used in this improved system.

Figure 19.6 shows the dependence of pressure fluctuation in a cell on current density in the situations of both Improved B-1 and AZEC® F-2 electrolyzers. F-2 has an upper duct that is different from the DAM-type overflow. The duct is separated

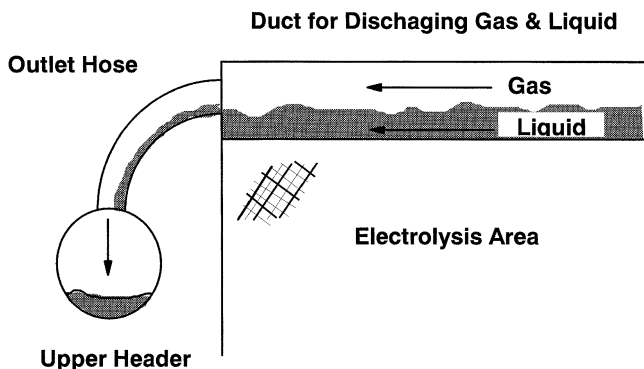


Fig. 19.5 Schematic of the smooth discharging system of AZEC® Improved B-1.

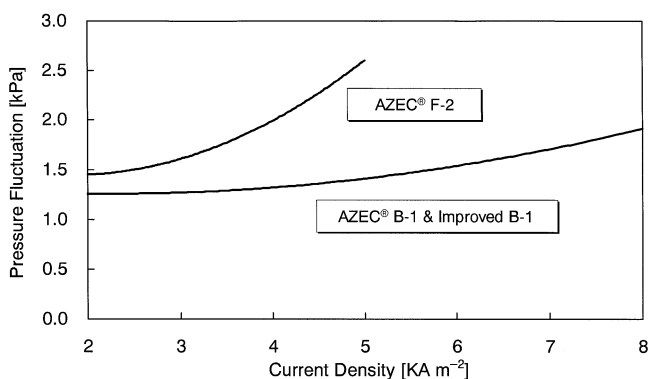


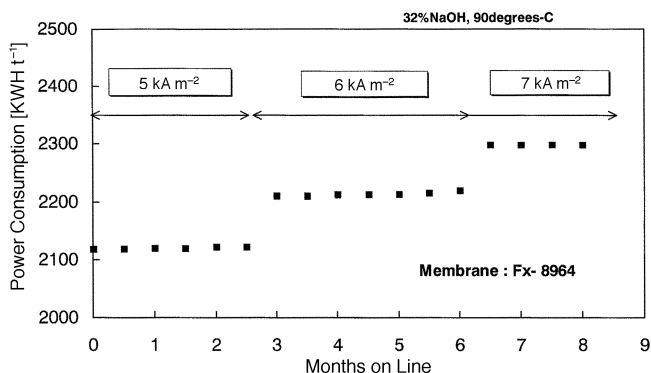
Fig. 19.6 Comparison of the pressure fluctuations in the cell between AZEC® Improved B-1 and AZEC® F-2.

from the electrolysis area by just a perforated plate. Figure 19.6 indicates that the DAM-type system of the Improved B-1 ensures no abrasion at the higher current density operation.

19.3.2 7 kA m⁻² test run by using a commercial-scale electrolyser

A commercial-scale Improved B-1, with a capacity of 10 000 metric tonnes per year (caustic base), came into operation successfully at the AGC Kashima factory in July 1999. Since then, the plant has demonstrated a long-run operation to prove its stable performance and durability under high current density. For the first 3 months, the electrolyser was operated at 5 kA m⁻². Then the current density was increased step by step up to 7 kA m⁻². An Fx-8964 membrane, which had just been developed as one of the optional membranes for high current density, was installed. The operation was observed to be stable for each current density. As is shown in Fig. 19.7, the power consumption at present is approximately 2300 (d.c.) kWh tonne⁻¹ at 7 kA m⁻².

Fig. 19.7 Performance of the AZEC® Improved B-1 electrolyser at the Kashima factory (NaOH production capacity of 10 000 metric tonnes per year).



Low oxygen content in chlorine gas with hydrochloric acid addition

In the Improved B-1 at the Kashima factory, low-oxygen content chlorine gas can be obtained by adding hydrochloric acid to the feed brine. Figure 19.8 shows the dependence of the oxygen content in the chlorine gas upon the content of the hydrochloric acid in the feed brine at 6 kA m^{-2} current density operation.

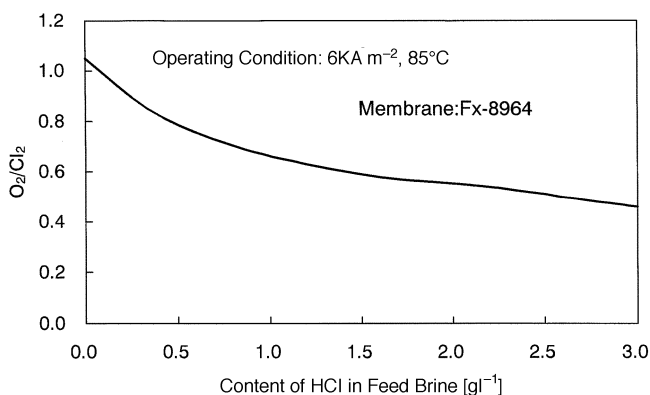


Fig. 19.8 Oxygen content in chlorine with hydrochloric acid addition to the AZEC® Improved B-1 facility at Kashima.

High quality of caustic soda produced

Figure 19.9 shows the dependence of NaCl and NaClO₃ in the 32% NaOH produced upon the current density value. A value of 3 ppm NaCl in 32% NaOH was measured as a remarkable quality of caustic soda at 7 kA m^{-2} .

19.4 Further developments for 8 kA m^{-2} operation

The mass transfer through the boundary layer on the membrane should be taken into consideration when designing both the cell and the membrane for use at higher current densities. The high rate of sodium mass transfer results in the depletion of

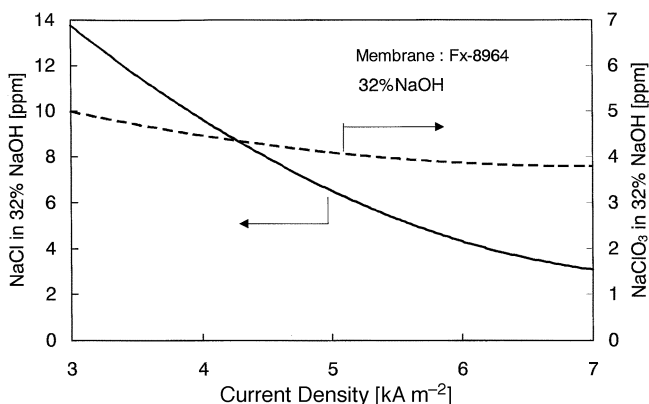


Fig. 19.9 Quality of sodium hydroxide in the AZEC® Improved B-1 facility at Kashima.

brine on the anode-side surface of the membrane and a rise in the caustic concentration between the cathode and the membrane surface. The AZEC® electrolyser has been provided with the previously described internal devices to ensure sufficient electrolyte mixing, which enhances the mass transfer.

Another requirement is a reduction in the generation of heat. Operation of any membrane under 90°C , even at 8 kA m^{-2} , is very much desired for safety reasons and to prolong the life of the cell, piping or any other facilities subjected to high temperature. The ohmic drop beyond the membrane has been previously lowered by the narrowed gap separating the electrodes. This leaves further reduction of the ohmic resistance of the membrane to be achieved.

19.4.1 Pilot-scale evaluation of 8 kA m^{-2} operation

AGC has developed the low ohmic resistance membrane (F-8934) for high current density operation up to values of approximately 6 kA m^{-2} . The new arrangement of the sub-structure of the membrane has contributed to wider distribution of the current passing through the membrane. This configuration decreases the actual current density localised over the membrane. Thus, the F-8934 shows 25% lower ohmic resistance than that for the F-893, as is shown in Fig. 19.10, even though the former comprises almost the same materials as the F-893.

The F-8934 seems attractive to any commercial plants operational in the range of $3\text{--}4\text{ kA m}^{-2}$. This membrane has already been supplied to such end-users. As a result, they have obtained a $30\text{--}40\text{ kWh tonne}^{-1}$ reduction in power consumption compared to the power consumption of the F-893 membrane. Figure 19.11 shows the current efficiency plots from two AZEC® plants in the current density range just touched on.

To date, the Improved B-1 with an F-8934 membrane has been operated as a full-sized pilot cell. Some essential data at 8 kA m^{-2} are in the process of being collected. Improved B-1 combined with F-8934 shows significantly lower power consumption, as is shown in Fig. 19.12. F-8934 shows a value of less than $2300\text{ (d.c.) kWh tonne}^{-1}$

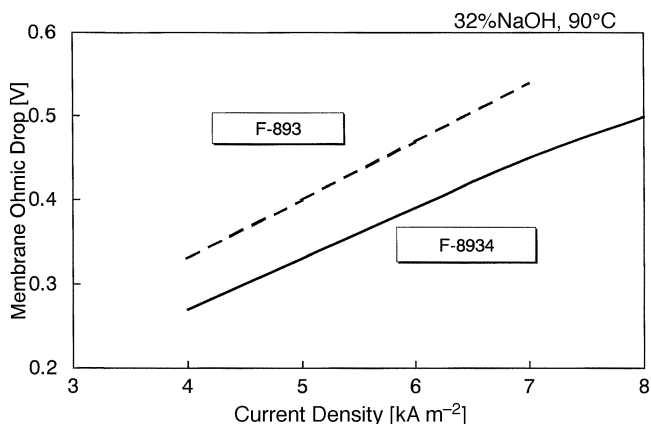


Fig. 19.10 The new low ohmic drop membrane, F-8934.

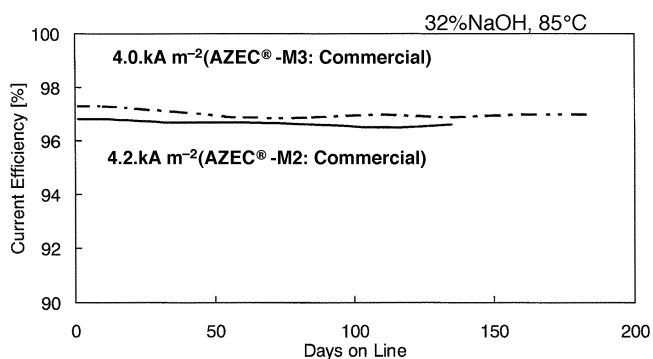


Fig. 19.11 Performance of the F-8934 membrane in AZEC® electrolyzers.

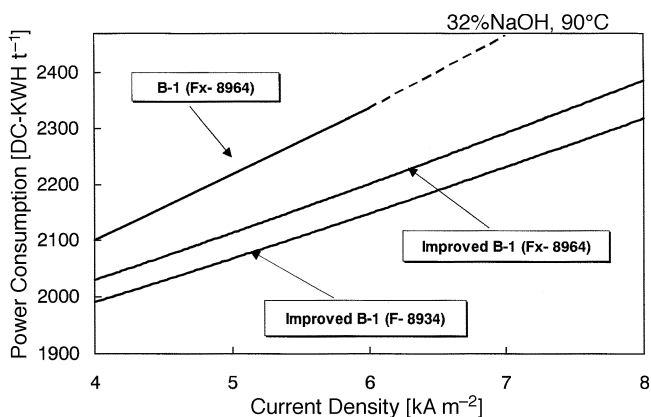


Fig. 19.12 Power consumption plots for the AZEC® B-1 and Improved B-1 electrolyzers.

power consumption, which is approximately $70 \text{ kWh tonne}^{-1}$ lower than that of the Fx-8964 in test cells operating at 8 kA m^{-2} .

All of the test runs at higher current densities in the pilot cells have been completed, or are presently ongoing, for just two months or so, the idea being to focus on the properties or the performance of the electrolyser and the membrane. The durability of

the membrane at 7 kA m^{-2} or higher will be determined, however. The F-8934 membrane is presently undergoing evaluation of its durability in full-scale cells.

19.4.2 Membrane for higher current density operation

Several test runs have been carried out using 1.5 dm^2 laboratory cells with the F-8934 at 8 kA m^{-2} . The current efficiency at 8 kA m^{-2} was about 1% lower than that at 5 kA m^{-2} , and no further decline was observed. F-8934 has also had a similar evaluation result in full-scale pilot cells at 8 kA m^{-2} . AGC has been obtaining slightly lower current efficiencies than its desired target of 97% at the beginning of the membrane lifetime. This has led AGC to ensure that the other stepped-up design concept should be applied to the membrane for 8 kA m^{-2} operation.

High current efficiency is provided by the sufficient rejection of hydroxide anion within the carboxylic polymer layer in the cathode side of the membrane. The rejection should be controlled by the proper size of the ion-conducting channels in the polymer layer. The channel size should depend on the relationship between the inner stress (pressure in the channel) and the elasticity of the polymer matrix. The inner stress will rise along with increased mass flux under higher current density. This possibly enlarges the channel size. To maintain a stable high current efficiency even during such conditions requires effective strengthening of the elasticity of the polymer matrix around the channel.

AGC has modified the carboxylic polymer and prepared one experimental membrane. This membrane is similar to F-8934 in the arrangement of the sub-structure, and it is almost the same as the F-8934 in both mechanical strength and ohmic resistance. Figure 19.13 illustrates the current efficiency trend of this experimental membrane in a laboratory test run at 8 kA m^{-2} , compared with the F-8934 tested under the same conditions. The absolute value of the membrane's current efficiency is approximately 97.5%. No decline in current efficiency has been observed. AGC is now evaluating the stability and is optimising the carboxylic polymer feature and fabrication process for commercial production of this type of membrane.

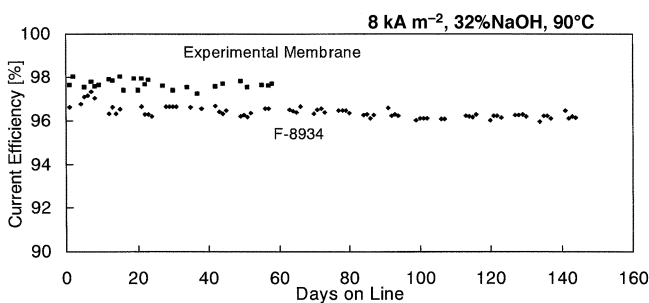


Fig. 19.13 Plot of current efficiency stability at 8 kA m^{-2} operation in a laboratory cell using the F-8934 membrane.

Chapter 20

A Dynamic Model of a Mercury Chlorine Cell

P W Masding and N D Browning

20.1 Introduction

ICI Chlor-Chemicals has four chlorine production sites: Lostock and Runcorn in the north-west of England, Wilton in the north-east and Wilhelmshaven in Germany. These sites operate a range of cell technologies including mercury, diaphragm and membranes.

This chapter concentrates on the mercury technology with waste brine system, as used at Runcorn and in particular a mathematical model of a mercury cell which is being used to improve the operability and efficiency of chlorine production. In general, however, the use of the techniques described here is applicable to all cell technologies.

A wide range of operating conditions and design philosophies affect mercury cell efficiency. For example, the fundamental distinction between a resaturation and a waste brine process influences the temperature and brine strength profile along the length of the cell and hence the overall efficiency. Another important factor is the quality of the brine. Impurities in the brine can cause base-plate deposits, which tend to reduce the anode/cathode gap. This gradual reduction in gap requires either manual or automatic adjustment and, eventually, the cell must be taken off-line and the thick mercury removed.

This list of factors influencing efficiency is by no means exhaustive; others include anode coatings and temperature limitations in the materials of construction. But perhaps just as important as efficiency factors inherent to the cells and raw materials, is the mode of operation imposed on the cells and in particular the stability of the load.

At present the UK electricity price varies every few hours during the day. A typical price distribution over a year is shown in Fig. 20.1. This variation in price exceeds a factor of ten and so clearly dramatically affects the economics of chlorine production. In the next few years this pricing structure is expected to change, but it is unlikely that it will become much more stable. A combination of this variable electricity price and

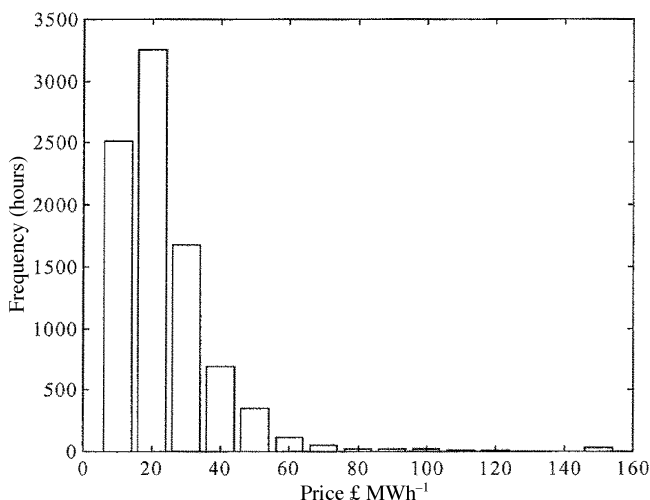


Fig. 20.1 Typical UK electricity price distribution.

other production considerations relating to a highly integrated manufacturing site, gives rise to the load distribution on the cellroom as shown in Fig. 20.2.

With this variable load and the generally complex factors affecting the mercury cell the task of optimising chlorine production is not easy. In a situation such as this a mathematical model of the process can be extremely useful. As a result ICI has taken advantage of a wealth of operational and experimental data for mercury cells, as well as experience in developing process models, to produce a dynamic model of a mercury cell.

The potential uses of a model like this are enormous. As with all dynamic models, the main advantage over plant trials is the much shorter time required to obtain results and the lack of risk to the plant in terms of production and safety.

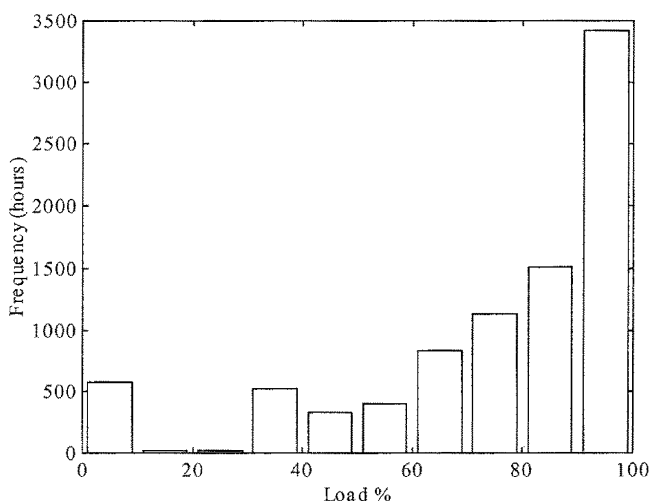


Fig. 20.2 Variation in plant load over a year.

Three applications of the model are described in this chapter:

- (1) Improved set-up of cells after base-plate cleaning.
- (2) Optimisation of raw and recycle brine flow as a function of load, using information on brine price and changing electricity tariff.
- (3) Improved control of k-factor and reduction of cathode/anode gap by developing a 'smart' low k-factor alarm which takes into account cell operating conditions.

All of these examples form part of live projects that were scheduled to be commissioned on the plant by the end of 2000.

This work is part of an overall instrumentation and control improvement strategy which is being pursued by ICI Chlor-Chemicals with the aim of reducing the amount of manual control required and improving energy efficiency.

20.2 Model background

The model is based on a proprietary dynamic modelling package so that no custom coding is required for basic functions such as integration and optimisation. This package uses a block structured approach to programming with simple individual blocks 'wired' together on the screen to produce the complex functionality of the whole model. This type of programming is ideally suited to process modelling where a number of identical units are often connected together and it is important to be able to see the overall structure.

At the heart of the model are the heat and mass balance equations governing the chlorine gas, brine and amalgam layers within the cell as illustrated by Fig. 20.3. At a more detailed level each cell is divided into eight zones. Conditions within each zone are assumed to be constant and there is a trade-off between model accuracy and execution time associated with the number of zones. Typically eight zones have been found to be a good compromise.

Figure 20.4 shows the interaction between one zone and the others as well as the internal heat and mass flows between the layers. Clearly a number of assumptions are made in writing any model such as this. For example, here it is assumed that the interface between the brine and chlorine is insulating so that there is no heat transfer between the two phases.

Heat and mass balance equations are used in all aspects of process modelling; however, what is key to this model is an understanding of the electrolytic process behind the cell. For example, the model must be able to predict current efficiency and k-factor if it is to predict electricity consumption. Most of these electrolytic parameters are calculated using empirical relationships derived from experimental data both from test cells and the full-scale plant. Considering k-factor, this is primarily a function of brine strength and temperature. Figure 20.5 illustrates the experimentally derived function used in the model.

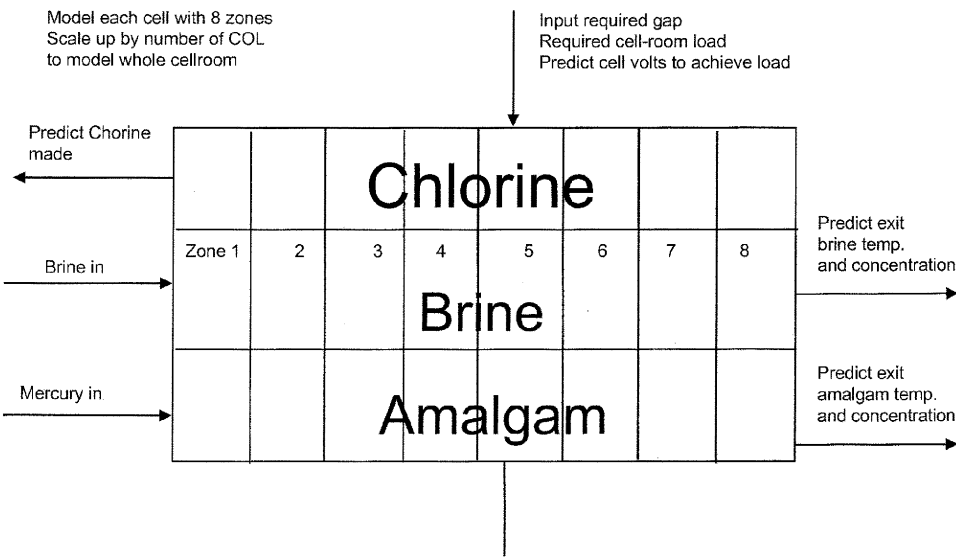


Fig. 20.3 The model divides the chlorine, amalgam and brine layers into eight zones for numerical integration.

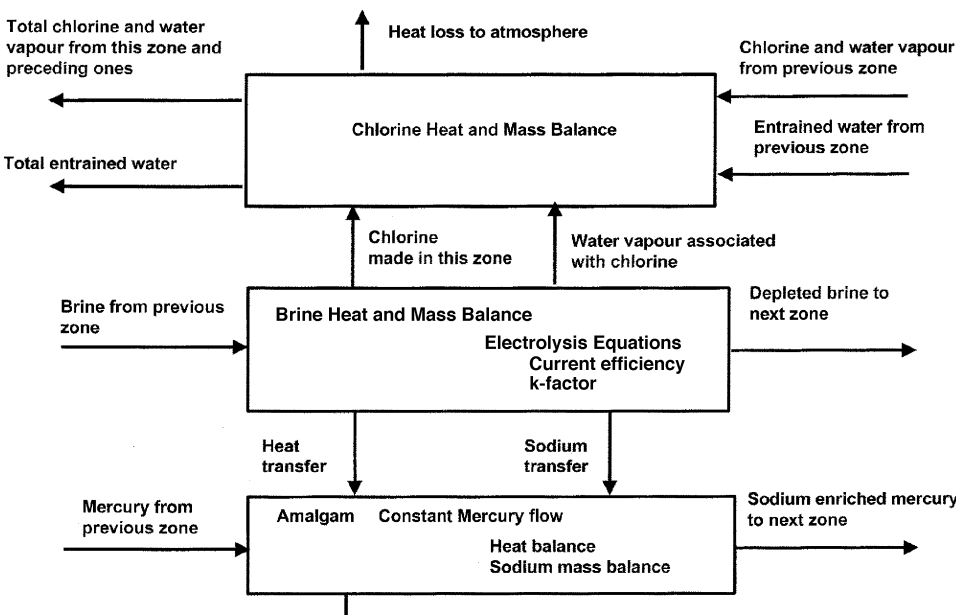


Fig. 20.4 Each zone has heat and mass balance equations and empirical relationships to describe the electrolysis.

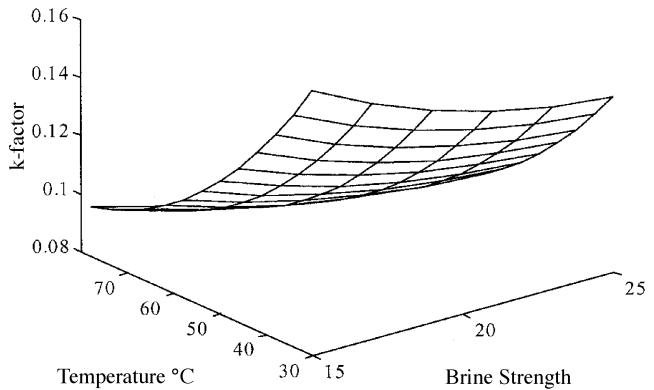


Fig. 20.5 The experimentally derived function for k-factor.

20.3 Model validation

Before the completed model could be put to work it needed to be tested against data from the plant covering a wide range of operating conditions. The test results were judged against clearly defined success criteria that take account of the proposed applications. In particular the accurate prediction of k-factor and exit brine strength was considered most important.

Before considering the validation process in detail it is important to realise that the model considers only one cell and yet the particular cellroom under study at Runcorn has 106. This means that the model must predict average values of parameters for the whole cellroom rather than, for example, each individual k-factor.

Figure 20.6 illustrates the test procedure. The key model inputs are defined at the left of the illustration and the outputs to the right. Only the essential input variables are shown here; others are in fact used by the model but they are either constant for all plant operating conditions or the model equations are not particularly sensitive to them.

The first objective of the test was to obtain plant input and output data for values of load covering the full operating range of the plant. Subsequently the model would be used to predict the outputs from the input measurements. Considering the input conditions, notice that some, such as inlet brine strength, will be common to all the cells, but others such as brine flow will not. This is because the position of each cell on the brine manifold determines the share of the total flow that it receives and although there are manual valves to bias these flows, a perfectly even distribution is never achieved. Now the model only represents a single cell and so it must attempt to predict average cellroom output values from average input conditions. The consequence of this observation is that the model can never be completely accurate because the relationship between inputs and outputs is non-linear.

Figure 20.7 illustrates this process for exit brine temperature. Here the distribution of brine flow from the main header, as well as the efficiency of each cell, influence individual cell exit temperatures in a complex and non-linear way.

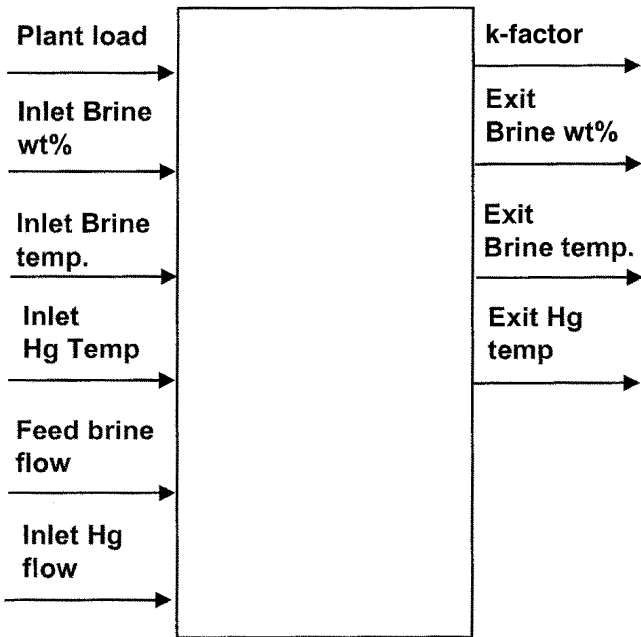


Fig. 20.6 Model inputs and outputs used for verification.

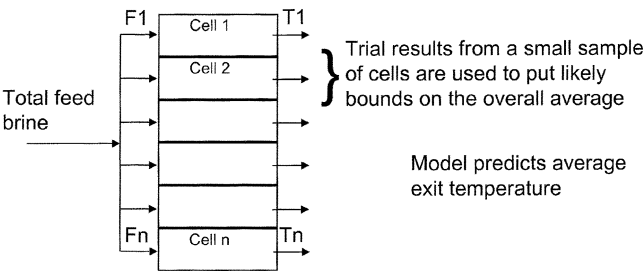


Fig. 20.7 Individual cell temperatures differ owing to factors such as brine flow distribution.

Another practical consequence of the large number of cells is that to sample the exit condition of all cells is extremely time consuming. As a result, in the case of exit brine strength for example, only a representative sample of cells was actually measured. The size of this sample was based on the variation in the individual measurements and statistical indicators that show how accurately the global average can be predicted from a small sample.

Table 20.1 summarises the model errors from the validation trials and shows that the model is successful in predicting the steady-state condition of the plant. Errors in waste brine strength and temperature must be compared with the total change across the cell which is about 13% for brine strength and 40°C for temperature. This is because the plant is a waste brine process; changes in brine temperature and strength are much smaller for a resaturation process.

Testing the dynamic performance of the model could not be done in such detail

Table 20.1 Model prediction errors.

Parameter	Low load	Medium load	High load
k-factor	1.1 points	2.9 points	2.1 points
Exit brine temperature	0.2°C	1.5°C	0.3°C
Exit brine strength	0.1 wt%	0.7 wt%	0.25 wt%

since many variables cannot be measured fast enough when the whole cellroom is continually changing. So only brine temperature was considered and the model was used to predict it in response to widely varying loads. Both temperature and load are continuously logged on the plant computer system making the task of data gathering for the trial very easy. Figure 20.8 illustrates the results of the test and shows that the steady-state accuracy of around 1.5°C for the brine exit temperature is maintained throughout the transient changes in load.

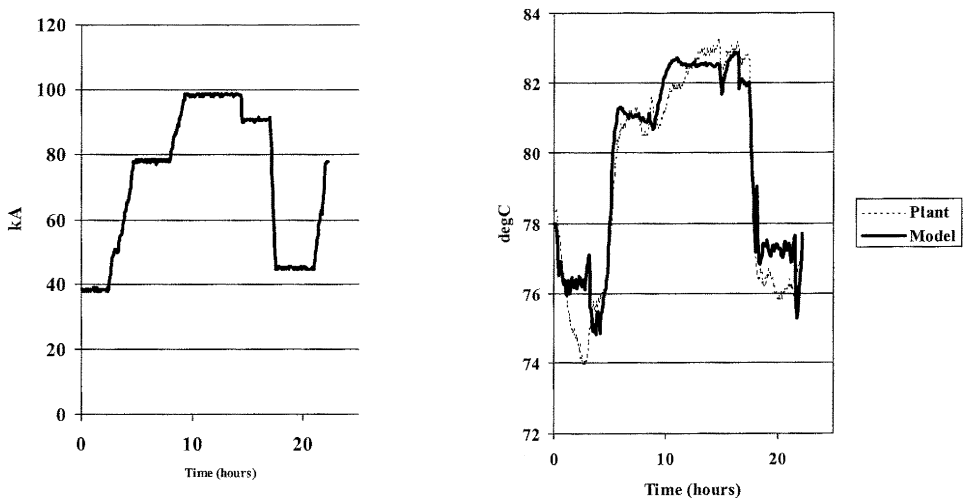


Fig. 20.8 Load variation affects exit brine temperature, but this can be predicted by the model.

With both dynamic and steady-state validation complete the model was ready to be applied to the plant.

20.4 Model applications

20.4.1 Cell gap adjustment program

Impurities in the brine cause deposits to gradually accumulate on the cell base-plate. As a result the cell must occasionally be flushed out and then put back on-line. When the cell is adjusted after a cleaning process the objective is to start-up with a particular

target anode/cathode gap. If this initial gap is set up either too large or too small then there is a price to pay: if the gap is too small then the interval before the cell needs readjustment is reduced with consequences for operator time. If, on the other hand, the gap is too large then the efficiency of the cell will suffer.

Setting up a cell would hardly be an issue if the gap could be measured directly but instead it must be inferred from k-factor. Because k-factor is dependent on a number of variables then these must be taken into account if the gap is to be accurately inferred.

To solve this problem a version of the model has been installed on a PC in the plant control room. Every time a cell is set-up the operators run the model and enter the prevailing plant load, total brine feed and brine temperature. They are then given a recommended cell k-factor profile to achieve the target gap.

The recommended profile is based on the model prediction for the average k-factor of the whole cell, but it is modified according to operating experience, which indicates which areas of the cell are subject to the quickest build-up of thick mercury. In the field the operators used hand-held k-factor probes to set the cell up according to the results from the model.

20.4.2 Brine/power optimisation

As previously mentioned, the mercury cellroom at Runcorn is operated as a waste brine process with some of the brine recycled through the cells. This process involves a trade-off between electricity and brine costs since with increased brine flow the cells operate at a higher average concentration, which saves power.

At present the operating practice is to set the fresh brine flow according to load alone and not take into account electricity cost. This clearly represents an opportunity to use the model to optimise the brine flows.

In this case the model is run in off-line mode and used to search for the raw and recycle brine flows which minimise the cost of chlorine production for a whole range of electricity prices and loads. Optimisation is simplified by the fact that the brine price is effectively fixed.

Figure 20.9 shows a typical optimisation trajectory found by the model for one load and power price combination. The starting point for the raw and recycle brine is based on current plant operating rules and appears as 100% on the flow axes. Subsequently the model varies the brine flows and runs to a new steady-state solution. The modelling package has a built-in optimisation routine which controls the searching process as dictated by the cost function, which is the price per unit of chlorine. In the case illustrated by Fig. 20.9 it requires eight runs to find the optimal solution.

Before implementing any optimisation on the plant it is important to know how much the total saving over a year might be to perform a cost-benefit analysis for the whole project. Plant records are available showing the load and power price on an hourly basis over a whole year as shown in Figs 20.1 and 20.2. In principle the model

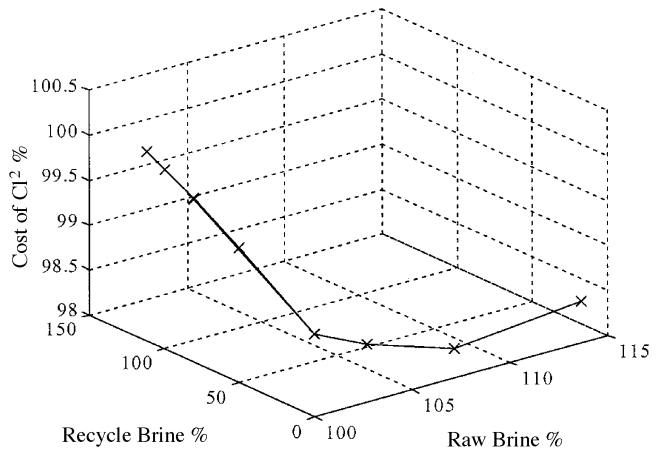


Fig. 20.9 A typical brine flow optimisation run.

needs to be run to optimise the brine flows for each of the load–power conditions and the total saving calculated. Even though the load and power prices do not vary every hour, however, the number of unique combinations is too large to make this approach practical.

In practice the solution is to divide the combinations of power price and load into a coarse grid covering the full range of both variables. In this case a 4-by-4 grid was chosen requiring that the model be run 16 times. Figures 20.10 and 20.11 show the results of this process. The surfaces indicated by these diagrams are the changes in brine flow from current base-case values which appear as 100% on the flow axis. As such they illustrate clearly that recycle brine needs to be reduced at all but the highest loads and that raw brine needs to be increased for combinations of high load and power price. These increases are quite large and show the dominant effect electricity price can have over any considerations of saving brine.

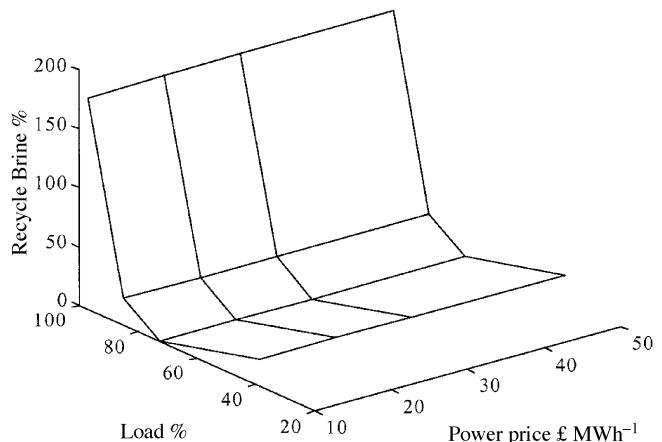


Fig. 20.10 Optimisation of recycle brine flow.

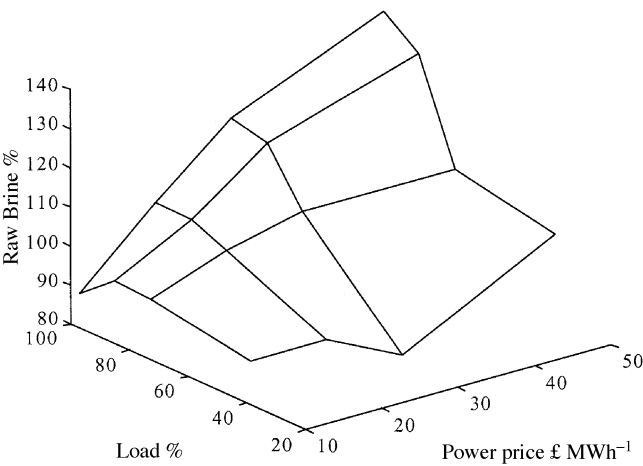


Fig. 20.11 Optimisation of raw brine flow.

Using the optimised chlorine production cost associated with these results and the base-case cost for the default brine flows then cost savings as a function of both load and electricity price are defined. This result is shown in Fig. 20.12 and it is the key to predicting annual savings from brine optimisation. To perform the calculation the saving associated with every power price and load combination that occurred throughout the year is obtained from the function in Fig. 20.12 by two-dimensional interpolation. These savings calculations were carried out by a separate mathematical package.

The result of this work with the model clearly shows that there are worthwhile savings to be had from brine optimisation particularly as the cost of implementation will be small. The plant already has a system which optimises its production schedule and the brine optimisation results can be added to the associated program in the form of a simple look-up table.

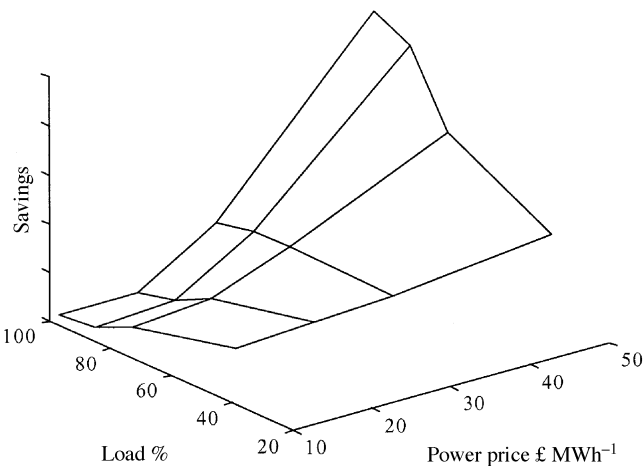


Fig. 20.12 Potential savings from brine optimisation over the full operating range of the plant.

20.4.3 Adjustable k-factor alarm

Since low k-factor is associated with a small gap then ultimately it can protect against the possibility of a cell shorting. The existing method used on the plant is a simple fixed low k-factor alarm which prompts the operators to increase the gap before any harm is done. Unfortunately k-factor is not a direct indication of gap and this means that any safety system based on it inevitably leads to conservative and sub-optimal operation.

To illustrate the problem consider Fig. 20.13. The aim of the alarm system is to trigger at some minimum safe gap. However, there is a whole range of k-factor values that can occur for that minimum gap which depends on the operating conditions of the cell. For example, factors which influence cell k-factor are its brine temperature and concentration. So to ensure that the gap never reduces below the safe minimum the alarm point must be set at the highest k-factor value which can never be associated with that gap which is the point KA on the diagram. This alarm point will then only be accurate at one set of conditions; for all others it will be wrong and will cause the alarm to trigger early when the gap is still above the safe minimum.

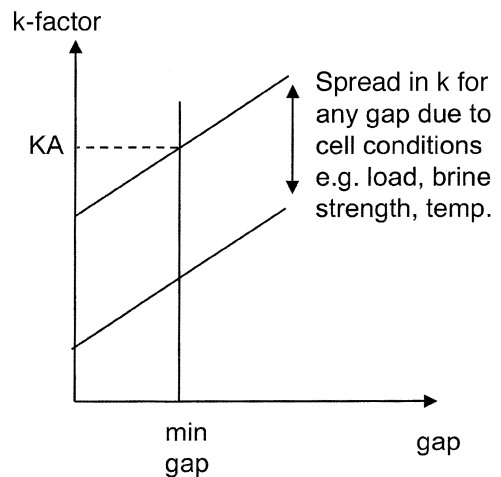


Fig. 20.13 A simple fixed low k-factor alarm system must be set at the point KA if it is to guarantee that the minimum gap constraint is not violated.

If the model is used then this situation can be improved considerably. In Fig. 20.14 some of the most important cell operating conditions are taken into account when inferring the gap from k-factor. This means that the spread of possible k-factor values that can be associated with that gap is reduced and the alarm point can be reduced from KA to KA' and yet still guarantee that the minimum gap constraint will not be violated. Notice that despite the use of the model there is still a range of gaps which could be prevalent when the alarm triggers. This spread is due to modelling errors and variables not used by the model.

Figure 20.15 illustrates the proposed implementation of this scheme on the plant.

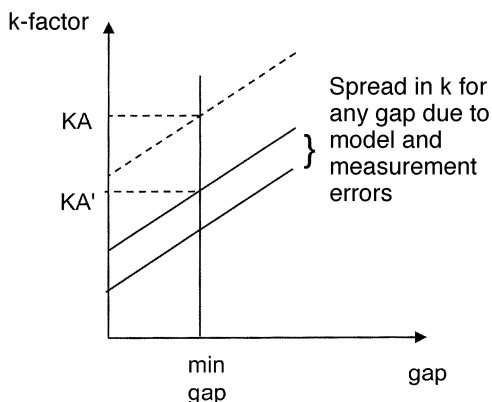


Fig. 20.14 A variable k-factor alarm system based on the model will allow the alarm point to be reduced so increasing efficiency.

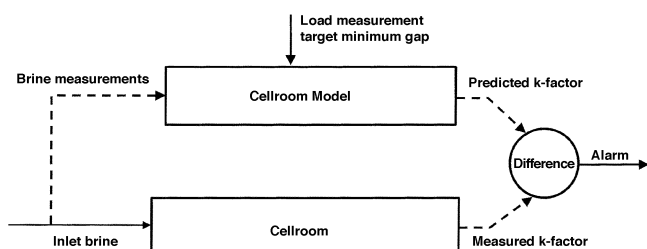


Fig. 20.15 Implementation of the variable k-factor alarm system.

Live plant measurements will be fed to the model via the plant control computer. The model will then use the measurements and the target minimum gap to predict the alarm trigger point which will be communicated back to the control computer. This control computer is a conventional distributed control system (DCS), which has all the necessary software and displays for alarm handling and recording. The model itself will reside on a separate PC. Communications between the PC and the DCS will be subject to error checking and the system will default to the old fixed alarm value if a fault is detected.

This application fully exploits the dynamic nature of the model since the alarm point will be modified continuously during load changes and other periods of non-steady-state operation.

20.5 Conclusions

The model of a mercury cell described in this chapter represents an effective combination of empirical data accumulated over several years of operation and theoretical heat and mass balance equations. Modern software tools and fast desk-top computers make the task of implementing the model relatively straightforward and of low cost so that it can be exploited for plant optimisation.

Model verification tests showed that it could predict k-factor to within 3 points

across the full operating range of the plant. Good accuracy was also obtained for exit brine strength and temperature.

The completed model has been a vital part of a programme of instrumentation and control improvement projects at the ICI Chlor-Chemicals Runcorn plant. It has been of assistance in all stages of the project including:

- identification of viable projects through its use for cost–benefit analysis
- fast assessment of a number of potential schemes in a way which minimises the number of trials required and hence any disruption to chlorine production
- use on-line in the final solution together with conventional control equipment such as distributed control systems.

Chapter 21

Ethylene Dichloride – Part of the Chlor-Alkali Plant?

I F White and R L Sandel

21.1 Introduction

If the pattern of chlorine use is analysed, it is apparent that it has changed greatly over the last few years. This is largely as a result of environmental legislation. Currently, the largest use by far is in the production of poly(vinyl chloride) (PVC). It is no surprise, then, that many of the largest chlor-alkali plants around the world have their production dedicated, either wholly or in the major part, to PVC plant or plants. At Washington, the term ‘vinyl chain’ is used to describe the following series of operations:

- (1) Electrolysis of brine to produce chlorine and caustic soda ‘by-product’.
- (2) Reaction of chlorine with ethylene to produce ethylene dichloride (EDC).
- (3) Cracking of EDC to produce vinyl chloride monomer (VCM) and hydrogen chloride ‘co-product’.
- (4) Reaction of hydrogen chloride ‘co-product’ with further ethylene by oxyhydrochlorination to produce additional EDC.
- (5) Polymerisation of VCM to produce poly(vinyl chloride) (PVC).

When appropriate, the chain is extended further upstream to include production of brine, for example by solution mining. Also, because the chlor-alkali plant is a major user of electric power, it is sometimes convenient to include the power generation plant within the chain. For the purposes of this chapter, however, the definition of ‘the vinyl chain’ shall be restricted to the five processes listed above (Fig. 21.1).

Conventionally, these five processes are grouped into three different plants. The chlor-alkali plant stands alone, as does the PVC polymerisation plant. The remaining three steps are often built as a single ‘vinyl chloride plant’, the so-called ‘balanced mode’ producing VCM from the feedstocks of chlorine and ethylene, with all the EDC and hydrogen chloride recycled within the VCM plant to extinction. In this chapter, the discussion centres on an alternative way of thinking whereby the EDC unit is

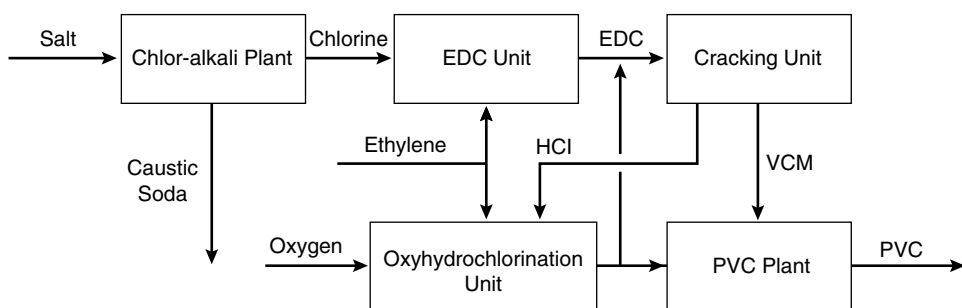


Fig. 21.1 Vinyl chain block flow diagram.

regarded as the final stage of the chlor-alkali plant, rather than the first stage of the vinyl chloride plant.

21.2 Chlorine consumption

Table 21.1, adapted from data in M.G. Beal's presentation at the 1997 SCI London International Chlorine Symposium, shows the pattern of consumption of chlorine in the USA in 1995 [1]. Figures for other markets or for different years will show some variation from this pattern. In the recent past, however, the high proportion of chlorine entering the vinyl chain is a feature of all major markets.

Table 21.1 End-uses of chlorine in the USA (1995).

PVC	40%
Propylene oxide	9%
Epichlorohydrin	5%
Phosgenes	10%
Solvents	4%
Fluorocarbons	4%
Other organic end-uses	8%
Pulp and paper	7%
Water disinfection	5%
Titanium dioxide	2%
Elemental chlorine	3%
Other inorganic end-uses	3%
Total	10 192 000 metric tonnes per year

Consider now the trends affecting the figures in Table 21.1. It is common knowledge that the use of chlorine for many purposes, notably for pulp bleaching and for synthesis of refrigerants, is steadily being reduced. On the other hand, PVC consumption shows a long-term growth pattern, albeit one that fluctuates according to the state of the global economy. PVC is, in fact, the only real contributor to the long-term growth predicted for overall chlorine consumption.

The historic and projected world data in Table 21.2 were presented by Tecnon at a seminar in Vienna in September 1999 [2]. During the ten-year period from 1995 to 2005 the chlorine contained in PVC is predicted to rise from 32.6% of net chlorine production to 42.2%. It must be pointed out that these figures slightly exaggerate the effect as Tecnon also predicts a growth in the quantity of chlorine recovered from HCl. Nevertheless, the overall trend is very clear. Over the period, chlorine growth averages 2.0% while PVC growth averages 4.7%.

Table 21.2 Actual and predicted growth of Cl₂ and PVC production over the ten years from 1995.

	1995	1997	1999	2001	2003	2005
Cl ₂ production ($\times 10^3$ tonnes)	38.0	39.5	40.3	42.0	44.5	46.4
Cl ₂ in PVC ($\times 10^3$ tonnes)	12.4	14.5	15.7	16.5	18.1	19.6
Percentage	33%	37%	39%	39%	41%	42%
Annual chlorine growth	—	2.0%	1.0%	2.1%	2.9%	2.1%
Annual PVC growth	—	8.1%	4.1%	2.5%	4.7%	4.1%

It is already the case that many chlorine plants operate exclusively, or almost exclusively, for the production of feedstock to the vinyl chain. The net effect of the increasing dominance of PVC as the ultimate product of the chlorine plant will be that many new plants will be directly linked with the vinyl chain.

21.3 The vinyl chain

The vinyl chain can be represented as follows:



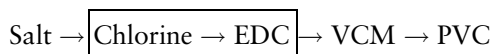
Both chlorine and, to a much lesser extent EDC, have other uses than the production of PVC. The diversion of some quantities of these materials as alternative products does not affect the validity of the concept of the vinyl chain. However, in this chapter, the chain will be treated as continuous without alternative products.

It is conventional practice to group EDC production with that of VCM, thus:



There is some logic for this grouping, which will be discussed later. The reasons though, are largely historical, derived from the practice of treating chlorine as a merchant chemical and the fact that EDC and VCM technologies are often the property of the same licensor. Also, chlorine has historically been treated as an ‘inorganic’ chemical, while EDC and VCM have been ‘organic’ chemicals. This is considered to be a somewhat arbitrary distinction.

The purpose of this chapter is to emphasise the merits of an alternative grouping, as follows:



For chlorine that is destined to enter the vinyl chain, it is believed that this grouping may make much better conceptual sense.

21.4 Storage and transport of liquid chlorine

Several factors are leading towards the elimination of storage and transport of liquid chlorine. Chief amongst these are:

- regulatory and legislative pressures regarding the control of major accident scenarios for chlorine storage and shipment
- economic pressures to eliminate, if possible, the high energy consumption needed to liquefy chlorine

The industry is well aware of the regulatory pressures to control and limit liquid chlorine shipment and storage and it is not the intent of this chapter to review them. Instead, the focus will be on some of the technical and economic aspects of eliminating liquid chlorine. If the EDC plant were to be combined with the chlor-alkali plant, taking vapour chlorine as feed, then the costly operation of chlorine liquefaction could be eliminated along with the hazardous storage and transport of liquid chlorine. Of course, elimination of liquid chlorine storage means that the EDC plant must be designed with sufficient flexibility to accommodate the normal variations in chlorine production rate, and it can.

The latent heat of vaporisation of chlorine is approximately 280 kJ kg^{-1} . The difference in enthalpy between compressed chlorine at a temperature of 50°C and liquid chlorine at -15°C is somewhat greater at about 305 kJ kg^{-1} . This energy must be removed to liquefy the gas for storage and the latent heat must then be added back when the liquid is revaporised. Even though it is possible in theory, it is rarely practicable to use any form of energy conservation in these two operations. In practice, chlorine is generally liquefied using a mechanical refrigeration system and revaporised against steam.

Mechanical refrigeration equipment used in chlorine liquefaction service typically absorbs about 110 kW for every 100 kW of cooling duty. Liquefaction of chlorine will, therefore, require some 335 kJ kg^{-1} of electrical energy. Converting this to the units used in comparing electrolyzers, this represents 83 kWh per tonne of caustic soda. When it is considered that the chlorine technology licensors distinguish their equipment with differentials of this same order, the benefits of eliminating lique-

faction become very clear. Additionally, this amount of heat must be sent to cooling water.

Furthermore, liquefaction efficiency will always be less than 100%. Some of the chlorine produced must remain with the non-condensable tail gas. The relevant factors were addressed in a paper presented at the 1997 SCI London International Chlorine Symposium [3]. In the processing of the tail gas, up to about 4% of the chlorine produced in the electrolyzers is diverted to lower value products such as bleach or hydrochloric acid. Small quantities of secondary products such as these materials can also present a marketing problem. A further loss of chlorine product can occur in the storage system, particularly in systems where padding air is employed.

Additionally, some EDC plants require a vapour chlorine feed. For this case, it would then be necessary to revaporise the liquid chlorine to feed it to the EDC plant. The steam required for the revaporisation is equivalent to an additional 70 kWh per tonne of chlorine. (It should be noted that the EDC plants designed using the technology of Washington's partner, OxyVinyls, can use either liquid or vapour chlorine feeds.)

21.5 Process economics

It is possible to place costings against each of these factors. Of course, the actual numbers will vary according to a producer's individual circumstances, but the orders of magnitude involved can be demonstrated. For all the calculations a plant producing 600 metric tonnes of chlorine per day (tpd) with an on-stream time of 350 days per year has been assumed. The entire chlorine production is assumed to be dedicated to the vinyl chain.

As noted already, the electrical energy needed to run the refrigeration unit for liquefaction of chlorine is about 335 kJ kg^{-1} , equivalent to 93 kWh per tonne of chlorine. The annual power consumption will be 19.5 million kWh. At a power cost of 5c per kWh, the annual cost is close to US\$1.0 million. There will also be an operating cost associated with the incremental cooling water usage that has not been included.

If a liquefaction efficiency of 97% is assumed, the hypothetical 600 tpd plant will 'lose' 18 tpd to tail gas. It is also assumed that the tail gas is diverted to production of sodium hypochlorite bleach with a sales value of US\$50 per ton of chlorine equivalent, while the chlorine feeding the EDC unit has a value of US\$180 per ton. The lost chlorine will cost the producer more than US\$800 000 per year. Even this figure ignores the facts that an equivalent quantity of caustic soda is consumed and that there will be a marketing cost associated with the bleach product.

It has been pointed out that the energy requirement for revaporisation, if required, is significantly less than that needed to liquefy the chlorine. The latent heat of 10 bar g steam is about 2000 kJ kg^{-1} , approximately 7.4 times greater than that of chlorine at

0°C; thus, a ton of liquid chlorine will need 140 kg of steam for vaporisation. The 600 tons of chlorine will need 84 tons of steam. At a representative steam cost of US\$10 per ton, this comes to around US\$300 000 per year.

There is clearly a significant investment cost in the equipment for liquefaction, storage and revaporisation of chlorine. Against this must be set the requirement for a separate thermal oxidiser, dedicated to vents from the EDC unit. Washington has developed an order of magnitude figure for the differential investment. This suggests that the capital savings associated with treating the EDC unit as part of the chlor-alkali plant could be as much as US\$10 000 per daily ton of production. This gives a differential of around US\$6 million for the hypothetical 600 tpd plant. (Even this figure does not allow for any incremental cost in steam and cooling water systems.) With even a low requirement for return on investment of 10%, these capital savings represent an equivalent annual saving of US\$600 000.

Whilst there are many other factors that would have to be taken into consideration, the four major components of cost savings developed in this chapter add up to a total annual saving of US\$2.7 million, as shown in Table 21.3, which is equivalent to US\$13 per tonne of chlorine. As can be seen, the economic incentive to delete the chlorine liquefaction is truly large. The question is how to do this in the most reasonable manner.

Table 21.3 The four major components of cost savings.

	Annual saving
Capital at 10% RoI	US\$0.6 million
Liquefaction energy	US\$1.0 million
'Lost' production	US\$0.8 million
Revaporisation energy	US\$0.3 million
Total savings	US\$2.7 million
Equivalent to	US\$13 per tonne of chlorine

21.6 Chlorine purity

Oxygen concentration is an important factor that must be considered in the safety design of an EDC plant, as is discussed below. Early membrane cell chlor-alkali plants could not be relied upon to produce low oxygen concentration or even a consistent high concentration. Nowadays, however, most of the chlor-alkali electrolyser licensors are willing to guarantee oxygen concentrations of 1% v/v or below during the full life of the membranes. Figures as low as 0.5% v/v have been quoted in certain instances. Even the 1% figure is within the acceptable range for the design of an economic EDC plant, but nearly any level of oxygen can be accommodated as long as it is stable and changes slowly. As will also be seen below, a small amount of oxygen is actually desirable in chlorine that is used to produce EDC.

21.7 Storage and transport of EDC

A number of reasons have been outlined, both environmental and economic, of why the transport and storage of liquid chlorine are not desirable. Combining the chlor-alkali plant with the EDC unit, as suggested, makes EDC the intermediate material in the vinyl chain. By looking at the physical properties of the two materials, shown in Table 21.4, additional reasons become apparent favouring EDC as the much preferred material for storage and transport. (As an additional comparison, the properties of VCM are provided as well.)

Table 21.4 Comparing the physical properties of chlorine and EDC.

Parameter	Units	Chlorine	EDC	VCM
Density	kg m ⁻³ at 0°C	1465	1283	945
Vapour pressure	bar at 0°C	3.665	0.028	1.750
Vapour pressure	bar at 25°C	7.81	0.106	3.98
Boiling point	°C at 0 bar g	–34	83	–14
Toxicity	—	High	Moderate	Carcinogenic
Corrosivity	—	High	Low	Low
Flash point	°C	—	13	–78

From the figures in Table 21.4, it is clear that EDC is a much simpler material to store and transport than chlorine. Because of its relatively low vapour pressure, EDC can be stored or shipped as a liquid at atmospheric temperatures and pressures. By and large, the physical properties of EDC are not too dissimilar from those of gasoline. It is apparent that tanks, pumps, etc. similar to those used for gasoline are suitable for EDC service, although care must be taken regarding the significantly higher density of EDC. The same comparison allows recognition of the relative simplicity of transporting EDC when compared to liquid chlorine. There is, however, one major issue with EDC storage and transport – that of handling the vent gases containing EDC vapour in an environmentally sound manner.

21.8 Hydrochloric acid

Vent gases containing EDC vapour, not only from the storage and transport of EDC, but also from the EDC unit itself, must be controlled because of EDC toxicity and other reasons. Conventionally these vent emissions are controlled using thermal oxidation, where the EDC vapour is converted to carbon dioxide, water, and hydrogen chloride. The latter is then scrubbed from the flue gases, resulting in a by-product hydrochloric acid stream. Consideration is required as to how this stream can be used or disposed of.

There are several places in the chlorine plant where hydrochloric acid is used, as follows:

- acidification of electrolyser feed brine
- regeneration of ion-exchange resin
- acidification of anolyte
- neutralisation of alkaline waste streams

The quality of acid required for these different uses will vary. Many electrolyser licensors will insist on the use of synthetic acid, at least for the first use listed. They are concerned about the contaminants that can be present in thermal-oxidiser by-product acid. Particular concerns are with iron and with organic materials; however, these contaminants can be removed with adsorption and other techniques, rendering the acid suitable for all but the most critical applications.

21.9 The OxyVinyls EDC processes

Washington has had a 40-year process technology association with the VCM licensor, OxyVinyls, designing EDC and VCM plants representing more than 60 licences and many more expansions and modernisations.

Together, the companies offer two versions of direct chlorination technology for producing EDC: low temperature and high temperature. Both of these direct chlorination processes can use either gaseous chlorine or liquid chlorine (or a combination of the two) in addition to the gaseous ethylene feedstock. The reactants are put into a solution of circulating liquid EDC containing generally a homogeneous catalyst. Both processes are typified by using natural circulation of the EDC liquid – pumps are not employed. Raw material efficiencies for both processes are similar and very high, typically well above 99% for both chlorine and ethylene.

21.9.1 Low-temperature direct chlorination

The low-temperature process, as its name implies, operates at a relatively low temperature where the exothermic heat of the direct chlorination reaction is removed by cooling water. The natural circulation is driven by the gas lift effect of the gaseous feeds before solution and the density differences of a cooler leg that has a relatively higher liquid density than the reactor leg.

Figure 21.2 shows the entire low-temperature process in block flow format. Following the reactor and cooler, the liquid EDC is washed, removing unreacted chlorine and catalyst. Product EDC is obtained in two distillation steps: drying, where water and a small amount of light by-products are removed; and purification, which removes a small amount of heavy by-products. Both of these distillation steps use steam-heated reboilers.

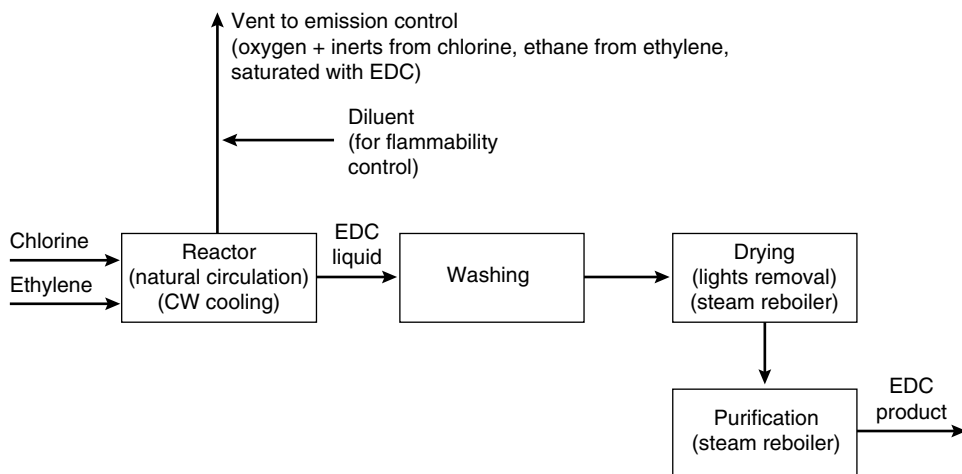


Fig. 21.2 Flow diagram of low-temperature direct chlorination.

21.9.2 High-temperature direct chlorination

The high temperature process, on the other hand, operates at an elevated temperature where the heat of the direct chlorination reaction actually vaporises a portion of the EDC. This reactor is also a natural circulation reactor, with the liquid EDC circulation driven by the vaporising material.

A major difference in the high-temperature process is that the EDC vapour is used directly to reboil the purification column, thus saving significant steam usage. Figure 21.3 shows the entire high-temperature process in block flow format. The reactor is directly connected to the purification column, where a small amount of heavy by-products is removed. Following that, the EDC is stripped of a small amount of light by-products, thus producing the EDC product.

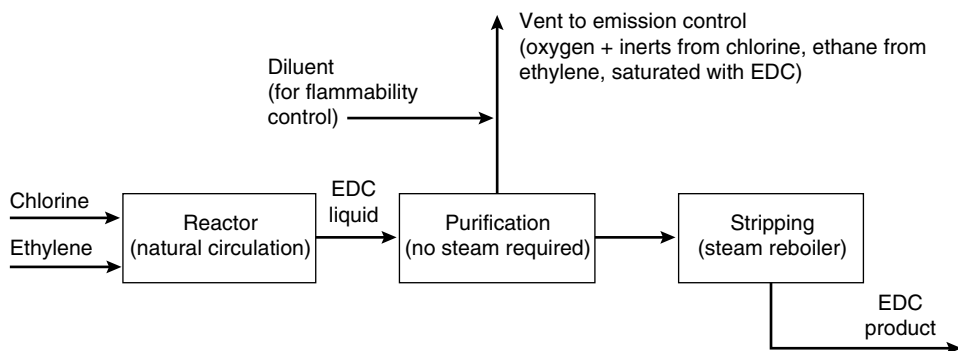


Fig. 21.3 Flow diagram of high-temperature direct chlorination.

21.9.3 Oxygen in the chlorine

In both processes, the vents from the reactor must be carefully designed. Actually, because of the high temperature configuration, the reactor vent in this process is from the overhead of the purification column.

The reactor vents are due to the non-condensables in both the chlorine and ethylene feeds. In the case of chlorine, the non-condensables are largely the oxygen and inerts (carbon dioxide and nitrogen) as produced from the electrolyzers. In the case of ethylene, the non-condensables are largely ethane, which is unreactive. The vent is also saturated with EDC vapour at the vent condenser temperature.

After recovery of the EDC, the vent gas contains both oxygen and fuels (ethane and uncondensed EDC) that would be a flammable mixture and a serious safety hazard if the plant were not designed and operated correctly.

The vent stream must be rendered non-flammable. Strategies used include either the addition of nitrogen, rendering the stream inert by bringing it below the lower explosive limit (6.2% v/v in air), or by adding a hydrocarbon fuel, to take the stream above the higher explosive limit (16% v/v in air). Where the vent stream is treated by thermal oxidation, then fuel gas is typically added and the second strategy used. If the unit is in an integrated VCM plant, ethylene can be added and the mixture recycled to oxyhydrochlorination where the contained oxygen and ethylene are reacted as feedstocks.

Interestingly enough, the oxygen contained in the chlorine feed actually has a real benefit. Around one-half mol% oxygen content is useful in the direct chlorination process where it limits the formation of by-products. In fact, when liquid chlorine is used as the feed, oxygen is often added for just this reason.

21.10 Overview

With modern EDC unit design, it is no longer necessary to provide a buffer of liquid chlorine between the chlor-alkali plant and the EDC or EDC/VCM plant. The EDC unit can easily and safely accept the gaseous feed of chlorine (after drying and compression) directly from the chlor-alkali plant.

The EDC unit design must accommodate the normal variations of chlorine production rates. This has been well demonstrated in commercial operation.

Physical separation of the chlor-alkali/EDC plant from the cracking/oxyhydrochlorination plant does create some complications regarding the necessary duplication of feedstocks and services. In particular, there will be the need for two ethylene supplies and for two independent thermal oxidation systems. Approximately half of the total ethylene must be provided as the feed to the EDC unit with the remainder fed to the oxyhydrochlorination unit. The EDC unit as well as the cracking and oxyhydrochlorination units will generate off-gases that require emission control,

generally by thermal oxidation. Physical remoteness of the EDC unit from the rest of the ‘vinyl chloride plant’ will dictate the need for separate thermal oxidisers. However, there are integrated producers that combine both the chlor-alkali and VCM plants at one location without either liquid chlorine or direct chlorination EDC storage that avoid these complications.

It should also be noted that there are some producers that have used the concept in this chapter where the chlorine production is combined with EDC production. The VCM plant would then be designed in the so-called ‘unbalanced mode’ where the feedstocks are EDC and ethylene, not chlorine and ethylene. Effectively, all of the chlorine and one-half of the ethylene come into the ‘unbalanced’ VCM plant as EDC. Frequently, the reason for this strategy is that EDC is very much easier and safer to store and transport than liquid chlorine. An additional important reason for this configuration is that chlorine can then be produced economically in areas of low-cost power. Often, these are the very same areas where low-cost ethylene is also available. Examples of areas of both low-cost power and low-cost ethylene are the United States Gulf Coast (see Fig. 21.4) and the Middle East.



Fig. 21.4 OxyVinyl's plant at LaPorte, Texas.

21.11 Conclusion

The decision as to where to locate the EDC unit in the vinyl chain depends on a number of complex factors. These must always be considered on a case-by-case basis. In this chapter the authors have attempted to provide a detailed overview of the impact of conceptually integrating the EDC unit within the chlor-alkali plant with a full summary of the benefits to the operator.

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Chapter 22

Back-pulse Filtration using GORE-TEX® Membrane Filter Cloths

M J Raimer

22.1 Improved brine treatment for new electrolyzers

In 1997 Bayer AG increased chlorine production at its Uerdingen site by adding Krupp Uhde membrane electrolyzers to the existing mercury cells. In order to achieve a high chlorine quality (minimum oxygen concentration) and maximum chlorine yield, the ‘acidic process’ is run – namely the brine leaves the cells at a low pH of 2.5–3.

To manufacture the brine, a vacuum salt is used to which the producer needs to add a small amount of anti-caking agent which forms a ferrihexacyanide complex in the brine. Because of the acidic process conditions, Fe ions tend to migrate into the electrolyzer membranes until encountering a sufficiently high pH and then precipitate [1]. This is an undesirable effect as it can cause void spaces within the membrane and thereby increase the voltage needed for the electrolysis. For this reason the ferrihexacyanide is depleted into $\text{Fe}(\text{OH})_3$ under well-defined conditions of temperature, residence time, free chlorine and pH in a process step prior to filtration [2].

Another brine species of high interest with respect to the cell voltage and membrane life is aluminium. In the electrolysis cells aluminium forms an aluminosilica complex [1] that can damage the electrolyzer membrane. This has a negative effect similar to that of iron migration in terms of power consumption. The necessity then of iron and aluminium removal (to mention only the most important elements) from the brine to their lowest possible levels is obvious.

The soluble ions of iron and aluminium are usually reduced to a minimum by adjusting the electrolyte pH. For the removal of solid iron hydroxide and aluminium hydroxide Bayer decided to use a new pre-coat-free brine purification technology – back-pulse filtration using GORE-TEX® membrane filter cloths.

22.2 The initial filtration method

For amalgam electrolyzers, Bayer was (and is still) using Kelly filters. In this type of filter it is usually possible to find several frames to which a filter medium made of

woven fabric is attached. Filter cake forms on the flat faces of the frames as fluid passes through the fabric medium. The frames are connected to pipes that lead to a filtrate header outside the filter. Before brine filtration can start, pre-coating with a filter aid is necessary. Bayer pre-coats the filters in the company's chlorine plants with alpha-cellulose which provides – after having formed a cake – excellent particle retention, so that the brine quality meets not only the specifications of the amalgam cells but also those of the new membrane electrolyzers.

In terms of filtration efficiency the Kellys provide adequate results, yet the major disadvantages of these filters are the relatively long downtime and the costs associated with cleaning the filters after each filtration cycle. At Bayer a typical filtration cycle (exclusive of pre-coating) is 8–10 days and involves switching the brine flow to another Kelly filter with the initial filter being shut down, emptied, opened up and cleaned manually with a high-pressure water jet. This procedure usually takes 4 h before the next pre-coating can begin. The total time spent off-line is typically 6 h.

When Bayer started the planning phase for its new membrane cell chlorine plant the company also evaluated new filtration technologies to eliminate costs for the use and disposal of filter aid and to reduce the cost of filter operation significantly.

22.2.1 Retrofit the Kellys or buy new filters?

The decision to retrofit or install new filters is influenced by plant-specific factors such as the condition of the existing filters, compatibility of the filters to retrofit, availability of space within the plant, etc. Bayer's analysis of the costs and benefits of the retrofit compared to the investment in new filters did not show a clear favourite; either decision could be justified. With regard to the rubber lining, gaskets, hydraulic system etc., the Kellys were in very good condition. Because of this, the decision was made to retrofit two of the filters and to use them in a separate brine circuit for the new electrolyzers, with a second circuit feeding the amalgam plant.

22.2.2 The set-up of the new filter system

The plastic frames with the filter cloth were removed and replaced by registers with filter tubes. Since the GORE back-pulse filter system requires a certain amount of filtrate to be pushed back through the filter media (see detailed explanation of the system below) the registers were constructed with a specific volume. Owing to the chemical conditions in the filter vessel, the registers had to be made of titanium, as it would have been impossible to manufacture a rubber-lined steel construction. Inside each Kelly filter, 256 'candles' are mounted at the bottom of the 17 titanium registers (Fig. 22.1). Each candle is 1680 mm (5.5 ft) long and 70 mm (2.75 in.) in diameter. The total filter area is approximately 90 m² (1000 ft²) per filter, which is sufficient for a total brine flow of 195 m³ h⁻¹ (860 US gallons min⁻¹).

Instead of the manual valves used in pre-coat operation of the Kelly filters, new ones activated by pressurised air were installed. The new filter system is connected to



(a)



(b)

Fig. 22.1 (a) Elevation view of a titanium register; (b) plan view of a titanium register arrangement.

the plant control system. All valves and instruments can be monitored in the control room. Manual control of each valve in the system can be completed with a mouse-click.

22.2.3 Filter cycle description

A filter is filled with raw brine until the registers are covered. The cycle automatically advances to the filtration mode and filtered brine is fed forward to the ion exchangers. After 2 h of filtering, the brine flow is switched to the second filter and the first one is back-pulsed with only the filtrate contained in the registers. The back-pulse releases the thin film of solids on the surface of the GORE-TEX® membrane and the solids settle into the conical part of the filter. After 2 h in the settling mode, the sludge valve is opened for a few seconds and the filtration cycle starts again.

22.3 Experience and results

Each filter has demonstrated the capacity to filter the full brine flow of $195 \text{ m}^3 \text{ h}^{-1}$. The pressure drop through the filter medium is measured and monitored continuously. Typically, it is nearly constant over a 2-h filtration at $195 \text{ m}^3 \text{ h}^{-1}$. Back-pulse cleaning restores the initial pressure drop from cycle to cycle, with only a slow increase over time. After 12 months' running time, the initial pressure drop at the beginning of the filter cycle had increased by 0.6 bar. The filter membranes were chemically cleaned with 5% hydrochloric acid. After a cleaning time of 2 h the filter was started again and the pressure drop was less than 0.1 bar greater than that of new filter socks.

Since the installation of the retrofit, the brine quality has been monitored using different types of analysis (MS, ICP, EDX, etc.). The filtration efficiency of the GORE-TEX® membranes has always met the Bayer specifications, which are significantly less than 100 ppb iron and aluminium. The filter membranes were put into operation in August 1998 and continue in service at this time.

22.4 Back-pulse filtration principles

Having examined a case history in which back-pulse filtration of brine is being used successfully, it is useful to understand the principles of the technology. These principles, when correctly implemented, enable back-pulse technology to produce a highly polished brine solution in one process step without the use of pre-coat or other filter aids. The principles are related to the arrangement of the filter, the stepwise filter operating cycle, and the characteristics of the GORE-TEX® membrane itself.

The typical back-pulse filter is a vertical tank pressure vessel with a conical bottom,

similar to the Kelly filters discussed previously. Unlike the Kelly filter, the filter candles are mounted in a tubesheet and an enclosed dome serves to contain the filtered brine rather than the register boxes used in the retrofit of the Kelly filter. The filter candles comprise a GORE-TEX® membrane filter sock and a patented [3] CPVC fluted support element. The filter socks are secured to the support elements with an elastomer band (typically EPDM rubber) and a metallic clamp (typically titanium). The sealing arrangement is illustrated in Fig. 22.2, and is identical to that used in the retrofit situation.

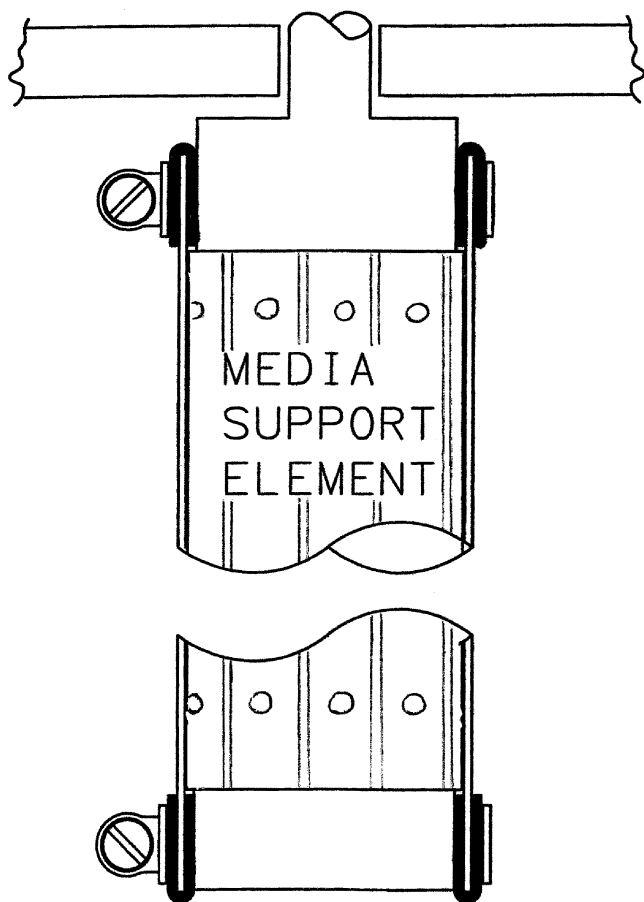


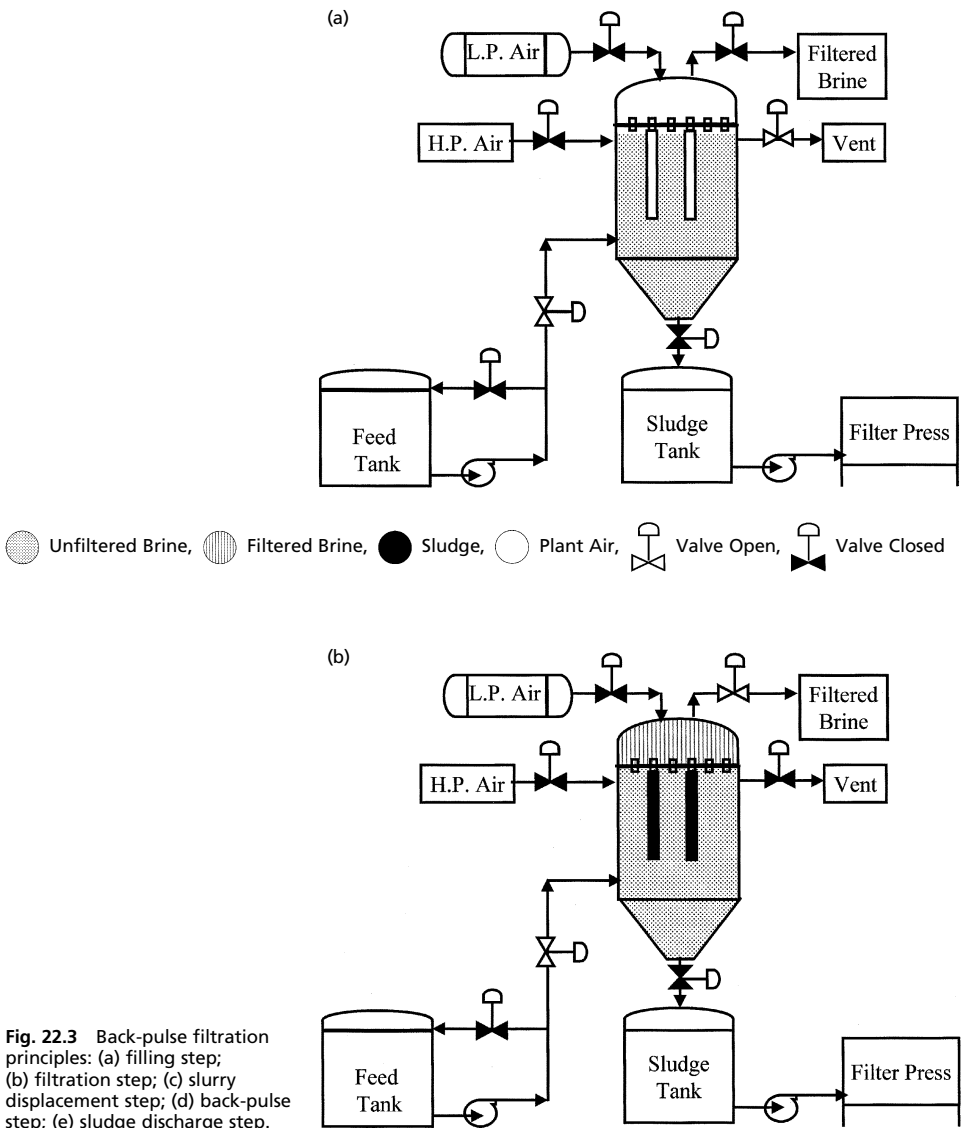
Fig. 22.2 Sealing arrangement of the GORE-TEX® membrane filter cloths on the support element.

The operation cycle is a stepwise process. The essential steps are filling the vessel, filtration (service), back-pulse (cleaning), cake settling, and sludge discharge. In practice, the steps will vary in length from application to application, but all working operation sequences include these basic steps, which will be addressed in order.

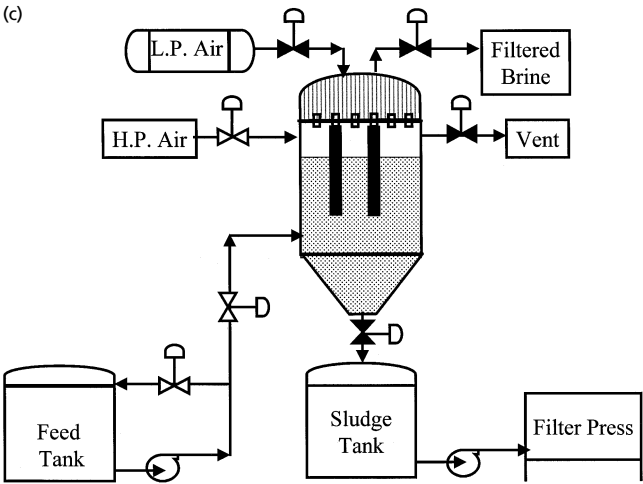
Filling the vessel is an obvious necessity, but because of the fine pore structure of the GORE-TEX® membrane (described below), air trapped in the vessel does not pass

through the membrane as it would through conventional filter media. An automatic valve is opened to vent the air and allow complete filling of the vessel with treated brine [Fig. 22.3(a)]. The filling step is terminated by a signal from a point-level switch mounted in an appropriate position in the vessel wall.

Once filling is complete, filtration begins [Fig. 22.3(b)]. Treated brine is pumped into the vessel at the desired flow rate through an automatic control valve. The flow of brine is from the outside to inside of the filter candles. Filtrate clarity is achieved immediately; no recycling of flow is required. As the filtration proceeds at constant flow, solids accumulate as a filter cake on the outside surface of the filter socks. While



(c)



(d)

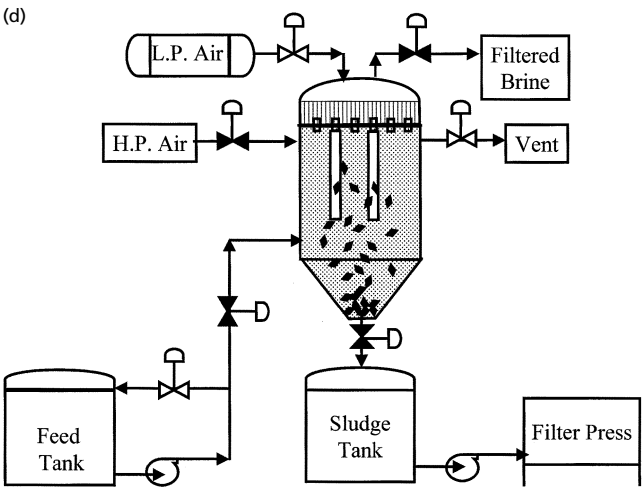


Fig. 22.3 Continued.

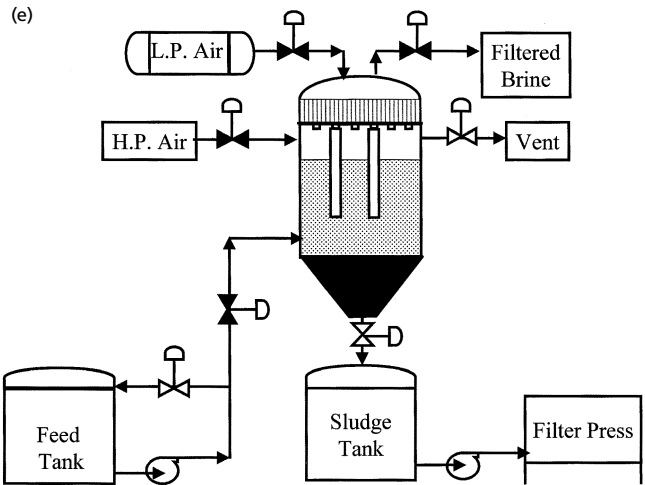


Fig. 22.3 Continued.

the filter cake thickens, differential pressure increases to maintain the flow set-point. A maximum differential pressure set-point or a timer terminates the filtration step.

22.4.1 Cake release by back-pulsing

The back-pulse is a short, sharp flow reversal that dislodges the filter cake from the membrane surface of the filter socks. It is the most important step in the sequence and its success ensures the success of the filter operation. As such, a clear understanding of the back-pulse step is critical.

During the pulse, a volume of the filtrate contained in the dome is displaced through the filter socks. To enable this volume to move quickly without the need for large external pipes, an equal volume of the unfiltered brine is first displaced from beneath the tubesheet [Fig. 22.3(c)]. Pressurised air is used to drive the unfiltered brine out of the filter vessel. The displacement is stopped when the fluid level in the vessel reaches an appropriately placed point-level switch. Once displacement is complete, the vessel is vented and low-pressure air at 0.3 bar is admitted to the dome. The air forces clean filtrate down through the filter socks, and the filter cake is dislodged from the surface of the socks [Fig. 22.3(d)]. In order to maintain a constant pressure in the dome as filtrate is pushed out, a separate low-pressure air reservoir supplies the necessary air volume. The back-pulse proceeds until the filtrate passing through the socks has refilled the vessel to the upper point-level switch, and is then terminated. The total time required for displacing slurry and back-pulse is typically less than 30 s, with the back-pulse itself requiring only about 5 s of the total.

The filtrate that is back-pulsed from the dome first expands the filter socks thereby cracking the cake. The movement of the socks and the subsequent liquid flow through them serves to dislodge the filter cake solids from the GORE-TEX® membrane surface. Because of the expanded PTFE material of the membrane, the cake releases from

it completely. The low pressure of the pulse imparts only a moderate amount of energy to the filter cake, thus avoiding a dispersal of the solids into fine particles and subsequent re-entrainment. The cake is maintained as large pieces having sufficient weight and density to rapidly settle through the unfiltered brine in the filter vessel.

The solids settle into the conical section of the vessel below the brine inlet line. This allows the filter to be put back into service without draining, thereby maximising the amount of time spent on-line. Depending upon the operator's requirements, several cycles' worth of solids can be collected in the cone and discharged periodically as thickened sludge thus minimising brine losses and/or recycle [Fig. 22.3(e)]. Sludge concentrations of up to 30% have been obtained in this way. Or, if circumstances permit, the filter can be partially drained after each cycle only to the extent needed to discharge the settled solids.

22.4.2 The filter medium: GORE-TEX® e-PTFE membrane

The final principles of back-pulse filter technology are the nature and properties of the GORE-TEX® membrane. The membrane is composed of expanded polytetrafluoroethylene, or e-PTFE. The membrane traces its roots to the invention of e-PTFE by Robert W. Gore in 1969. Since that time, e-PTFE has found application in many areas including medical devices, electronics, fabrics and fuel cells to name a few. In the filtration area, e-PTFE is used in the form of a membrane to capture and remove particles from both gaseous and liquid streams.

A scanning electron micrograph of a GORE-TEX® membrane for liquid filtration is shown in Fig. 22.4 at 1000× magnification. The membrane is composed of 'nodes' and interconnecting 'fibrils'. The resulting structure has very fine openings; the reference bar in Fig. 22.6 is 10 µm. At the same time, it has a large percentage of open

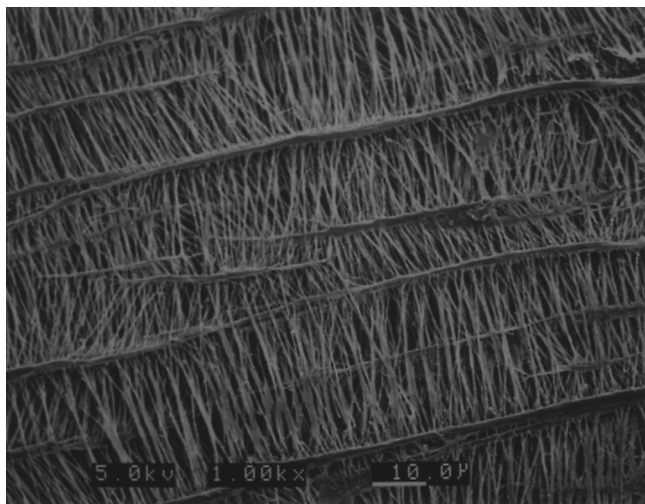


Fig. 22.6 Scanning electron micrograph of GORE-TEX® membrane at ×1000 magnification.

area available for fluid flow. This combination enables an extremely efficient filtration at practical industrial flux rates.

The fine structure of the membrane also allows 'surface filtration' to occur. Suspended solid particles are retained on the surface of the membrane and are not allowed to penetrate into or through the supporting felt cloth. In contrast, conventional media depend upon 'depth filtration' in which particles are retained within the medium itself. The results are immediate filtrate clarity without the need to build-up a filter cake, and reduced accumulation of solids within the medium that leads to increasing pressure drop.

22.5 Summary

Back-pulse filtration of brine using GORE-TEX® membrane filter cloths has been successfully implemented at chlor-alkali and sodium chlorate plants world-wide. The case of the Bayer chlor-alkali plant at Uerdingen, Germany has been reviewed in detail in this chapter. At Uerdingen, retrofit of Kelly filters to back-pulse operation has resulted in high brine quality (<100 ppb TSS) and a significant reduction of costs for maintenance, filter-aid purchasing and disposal.

The success of this and the other operations derives from the correct application of back-pulse filtration principles, in particular the back-pulse step itself in which the filter cloths are cleaned and made ready for further filtration. The properties of the GORE-TEX® membrane, composed of expanded polytetrafluoroethylene, give rise to the desirable results of these brine filtrations, in particular:

- highly efficient removal of suspended solid particles immediately after starting-up the filtration
- performing the particle removal in a single filtration step
- achieving this removal without the use of filter aids
- significant reduction of maintenance costs compared with conventional pre-coat filters
- long life through cleaning of the membranes with HCl, which restores the membrane to an as-new condition.

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Chapter 23

Cost Saving in Chlorine Plants by Benefiting from the Unique Properties of Titanium

A Ullman

23.1 Introduction

In this chapter brief information on the origin and cost of titanium will be discussed. A definition of the term ‘unique properties’ will be given and how these properties are exploited in the membrane, diaphragm and in the mercury cell processes will be considered and miscellaneous applications touched upon. The chapter will conclude with a summary of the financial benefits which, after all, propel the use of this challenging material.

23.2 Origin and cost of titanium

Titanium is not a rare material and it ranks as number four in abundance in the earth’s crust. Deposits in the form of rutile are spread all over the world and more than 95% of purified titanium dioxide is used in pigments, where its extraordinary stability justifies use for most qualified applications in the paint and paper industry.

The small fraction of titanium dioxide converted to metal passes through a chain of elaborate processes that aims at producing highly pure titanium in the form of ingots, slabs, etc. which may then be further processed to ‘semis’ such as sheets, tubes, bars, etc.

The total annual production of titanium in 1999 amounted to 50 000 tons of which 24 000 tons were alloyed with aluminium, vanadium and other metals to enhance strength and fatigue properties for use of titanium alloy in the aerospace industry.

The balance of 26 000 tons was processed mostly to sheet and used in the chemical industry and other applications where uptime has a value that is sufficiently high to justify the substitution of standard materials with titanium.

The current price of titanium is US\$15–20 kg⁻¹ in its unalloyed form and owing to its low specific weight, when compared with stainless steel, the relative cost per metre of pipe is US\$9–12 kg⁻¹, which is important to bear in mind when comparison is made with high-molybdenum stainless steels, which are today priced at around US\$9 kg⁻¹.

23.3 Unique properties

Titanium has a number of unique properties. In this chapter the focus will be on the corrosion resistance of the metal, which in turn is related to one of titanium's particular properties: the never-ending love affair between titanium and oxygen.

The high affinity between the two elements results in a ductile, strong and self-repairing oxide layer, and it is this layer that gives the titanium its unique performance. Titanium is a reactive metal and without the oxide layer it would simply dissolve in water.

The unique design properties of titanium are:

- corrosion resistance
- light weight
- erosion resistance
- high specific strength
- low thermal expansion
- good heat transfer

In the chlor-alkali industry titanium brings its properties to application as a material in activated metal anodes. In fact this is the major use of titanium in the chlor-alkali industry.

Figure 23.1 shows a Krupp Uhde membrane cell anode that makes use of titanium. Titanium itself cannot pass any anodic current until the breakdown voltage has been reached. This voltage in normal brine at its natural pH ranges from 7 to 14 V, the value depending on the purity of the metal, the quality of the brine, etc. Such a high voltage barrier would be highly impractical in commercial use, so it is overcome by merging the titanium oxide with a noble metal oxide having the same type of crystal structure. This allows the oxides to merge and provide a real mixed oxide. This mixed

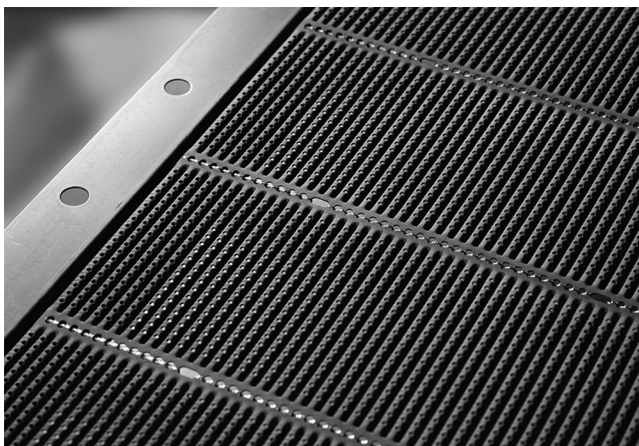


Fig. 23.1 Membrane cell with anode louver.

oxide constitutes the Beer coating for the electrode in the electrolysis cell and was discovered in the late 1960s.

The principal advantage of the Beer coating, which is commercially available under the tradename of DSA[®], is its unique adherence to the base metal of the electrode because of the titanium oxide part of the coating. Refined DSA[®] coatings of today have little in common with the first ruthenium Beer coatings.

Consider now Figs 23.2–22.7, which are based on the work of the French chemist Pourbaix, who plotted voltage against pH for a number of metals.

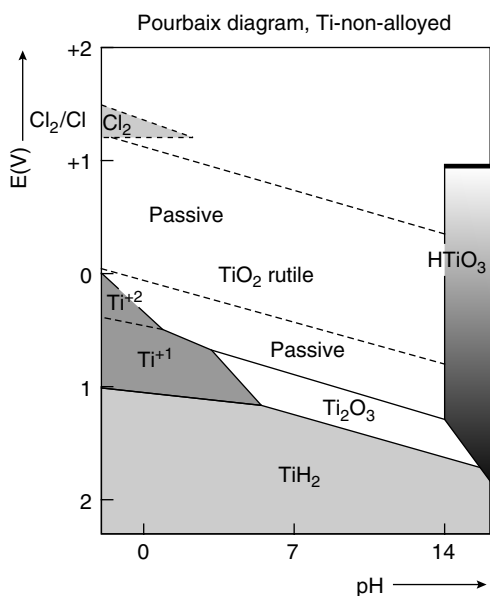


Fig. 23.2 Pourbaix diagram for non-alloyed titanium.

For most pH values and at most potentials, titanium is passive and no corrosion takes place. This is revealed by the white areas of Fig. 23.2. However, there are some exceptions. Consider alkaline attack (Fig. 23.3). It is occasionally assumed that titanium cannot be used in the alkaline conditions of hypochlorite and excess alkalinity, etc. Corrosion data do not sustain this assumption. It is only at high temperatures and high concentrations that corrosion becomes a factor of concern, as does the increase in erosion under such conditions.

Another exception to perceived wisdom is the reaction of titanium at low pH under reducing conditions. Consider a flange in an anolyte line (Fig. 23.4):

- with hot brine (90°C)
- with saturated with Cl_2
- a high E_{redox}
- a low pH

Area of alkaline corrosion at high temperatures

Alkaline attack of Titanium depending on temperature and caustic concentration

10% NaOH	20°C	0.001 mm a ⁻¹
30% NaOH	20°C	0.003 mm a ⁻¹
10% NaOH	100°C	0.02 mm a ⁻¹
30% NaOH	80°C	0.05 mm a ⁻¹
40% NaOH	80°C	0.13 mm a ⁻¹

Titanium not suitable at high temperatures

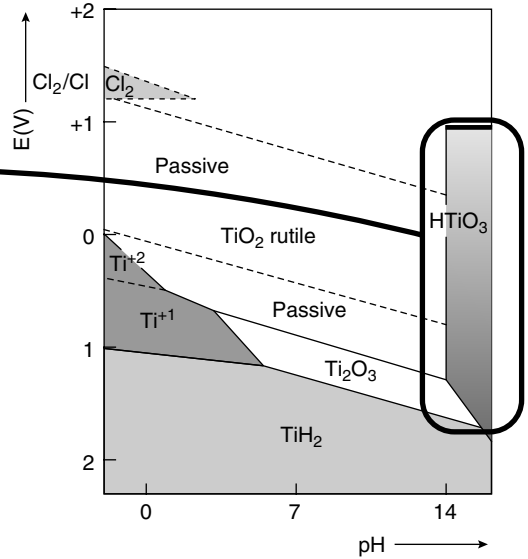
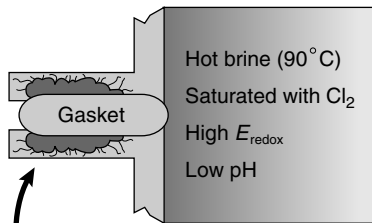


Fig. 23.3 Area of alkaline corrosion at high temperatures.

Area of crevice corrosion



In the crevice between Ti-flange surface or gasket material:
decreasing oxidising power
accelerating drop to pH
instability of passive layer
dissolution of the passive layer:
corrosion
hydrogen embrittlement:
TiH₂ formed

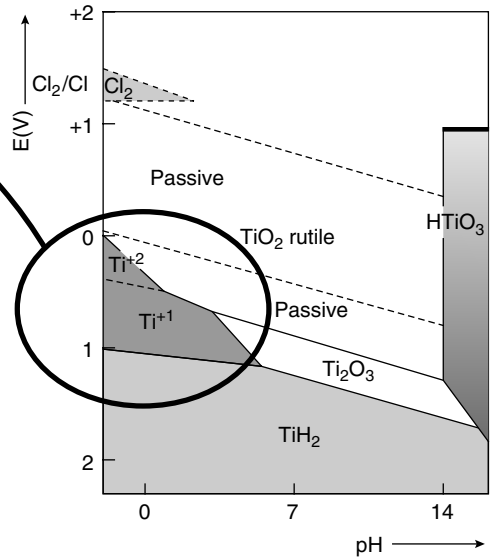


Fig. 23.4 Area of crevice corrosion.

Area of hydrogen embrittlement

Nature:

Cathodic currents causing titanium hydride formation and embrittlement.

Countermeasure:

Stray current dumpers (SCD) with proprietary coating applied in interlayers. The system and the coating composition is designed to promote hydrogen evolution at low overpotentials and to protect the titanium metal phase.

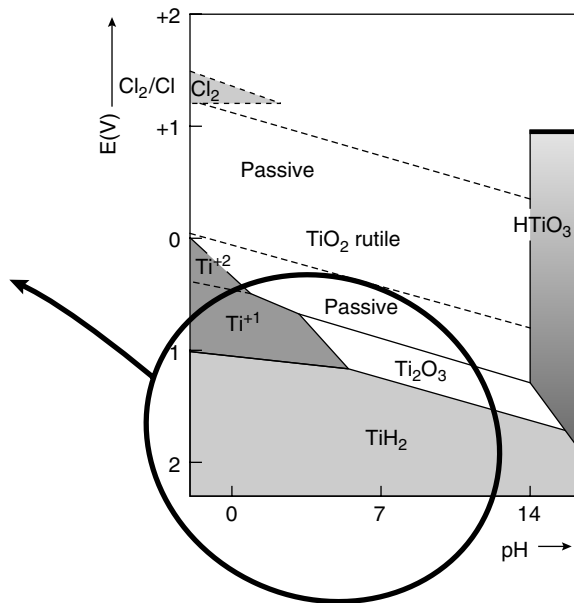


Fig. 23.5 Area of hydrogen embrittlement.

Area of anodic breakdown

Nature:

Too high anodic potential, i.e. by leakage currents, causing excessive growth of titanium dioxide layer. Eventually leading to a break away.

Countermeasure:

Stray current dumpers (SCD) with proprietary coating, which eliminates hazardous overpotentials.

Appropriate design of the system is essential.

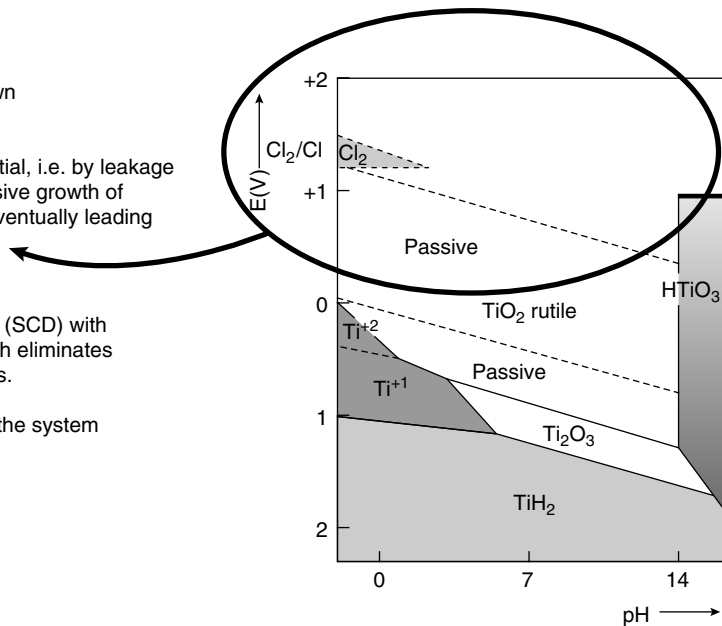


Fig. 23.6 Area of anodic breakdown.

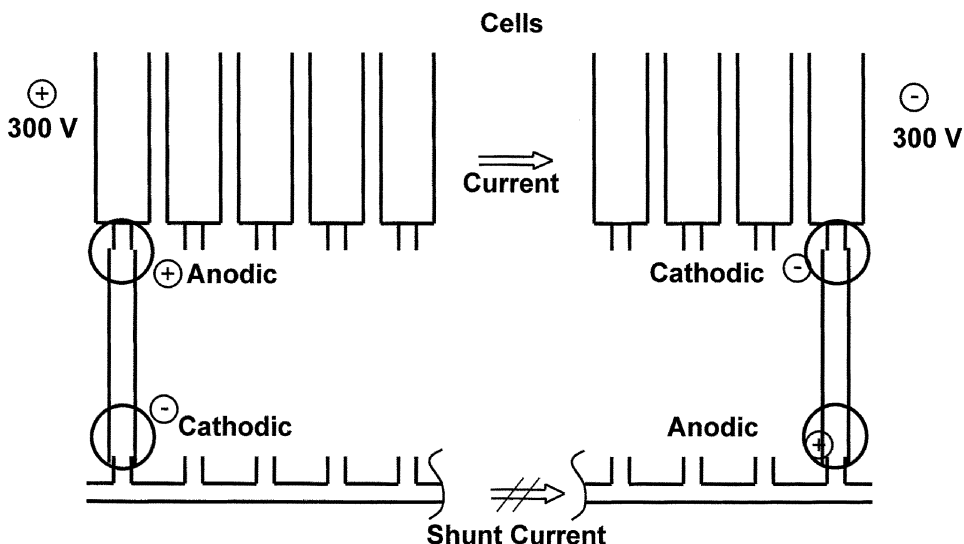


Fig. 23.7 Shunt currents, local anodes and cathodes due to electrolysis and cell design.

In the crevice between the Ti flange surface or gasket material it is possible to encounter:

- decreasing oxidising power
- an accelerating drop in pH
- instability of the passive layer
- dissolution of the passive layer (corrosion)
- hydrogen embrittlement (formation of TiH_2)

However, there are ways and means to circumvent these problems – but quality design features are important.

Titanium is alloyed either with palladium or ruthenium, sometimes with nickel and molybdenum, to increase the strength of the grain boundaries in the flange. However, this is a very costly route, especially in light of present palladium prices. Nevertheless, Permascand has developed a commercial system of noble coatings applied by electrochemical or thermal methods. Such coatings have been utilised for more than two decades and possess the ability to survive normal gasket changes.

Suppressed voltage is a normal condition in electrochemical plants, but it does require some attention. In this respect, consider cathodic polarisation. Although titanium is excellent operating as an anode, it has some shortcomings when operating as a cathode. The main reason for this is the formation of voluminous quantities of titanium hydride, which apart from spalling off, renders the cathode material brittle, resulting in crack propagation (Fig. 23.5). It is evident that hydride formation has to be prevented.

The most efficient method is to design a cathode with reduced polarisation exposure, providing shorter periods of high-intensity polarisation or longer periods at lower current densities, which can also be tolerated provided the correct protective layer is applied. Again, a set of catalytic coatings will lower activation energy at the cathode surface ensuring that the release of hydrogen gas is at such a low overvoltage that hydride formation occurs at a very slow rate.

Excessive anodic overvoltage at the catalytic coating must also be tackled (Fig. 23.6). This may lead to excessive titanium dioxide growth, eventually leading to breakdown. Such overpotentials can be countered by using titanium stray current dumpers.

Figure 23.7 illustrates a model of a membrane cell header where the battery voltage can be as high as 600 V. By proper design of titanium-based electrodes, this voltage can be reduced.

The purpose of Figs 23.2–23.7 is to indicate that selective use and proper design of cell units can optimise the unique properties of titanium.

23.4 Applications

23.4.1 The membrane process

Typical areas where titanium has found widespread industrial use in membrane technology are cells, anodes, anolyte headers, anolyte containers, filters, heat exchangers, chlorate removal systems and various parts of the brine system.

Many chlorine producers are having to tolerate impurities originating from standard plastic materials used in membrane technology. Hot chlorine and hot anolyte emerging from the anodic compartment of the cell place tremendous stresses on these plastic construction materials.

Chlorine reacts readily with most plastics, except for those comprising highly fluorinated polymers. Chlorine by-products from these reactions not only combine with the chlorine stream but also accumulate in the plastic material itself. This poses disposal problems when handling the contaminated plastic and ensuring its safe destruction with increasing numbers of restrictions being raised against large chlorinated molecules entering the environment.

Furthermore, a cell header with its 70–100 connections is not easy to replace, and considerable numbers of safety features have to be incorporated into its design. Composite materials do not lend themselves to effective non-destructive testing and a leaking joint may lead to delamination of the chemical-resistant liner from its mechanical support. Since any leaks cannot be detected easily in such circumstances, the entire header must be replaced with a corresponding electrolyser downtime.

A titanium system, properly designed with stray current dumpers (Fig. 23.8), will perform the necessary tasks of the cell header and is comparatively easy to repair in



Fig. 23.8 A titanium header.

case of damage. Titanium systems have been in use within Akzo Nobel for more than 15 years and no wear has so far occurred. The basic principle of the header is to collect stray current by use of several redundant stray current dumpers. In Fig. 23.9, the stray current dumpers are located within the small flanged nozzles, and a mesh basket is located in the large pipe working as a second 'line of defence'.

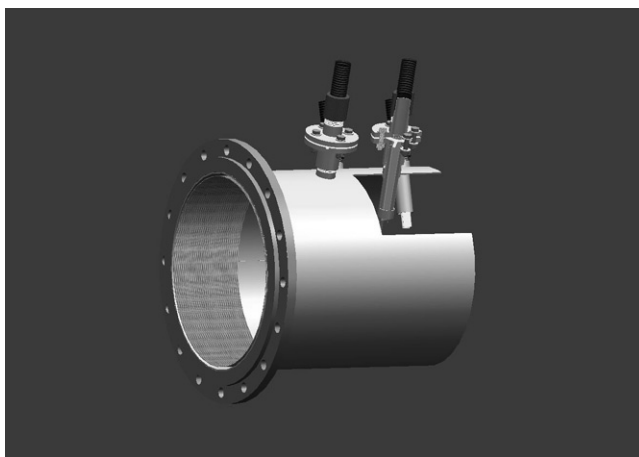


Fig. 23.9 A stray current dumper.

An increasing number of rubber-lined filter vessels are either retrofitted with Ti lining (Fig. 23.10) or are replaced by a solid titanium vessel (Fig. 23.11). The reason for this action concerns the sensitivity of the membrane to impurities, among which is iron. All sources of impurities are gradually being tightened up and an important use for titanium is as a spacer or frame in retrofitting existing filter frames when converting cellrooms to membrane technology.

Titanium mesh and other light and strong foraminous frame constructions will

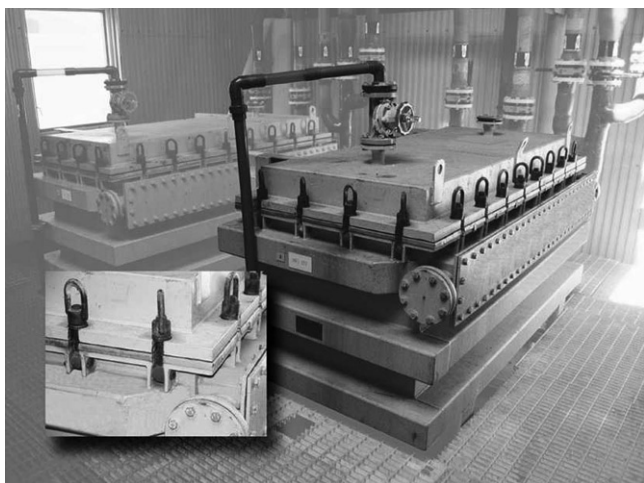


Fig. 23.10 The Scheibler filter with titanium lining.



Fig. 23.11 Solid titanium box-type filter.

support the filter cloth, thereby increasing the active surface of the membrane (Fig. 23.12). A recent development of classical filtering is represented by membrane filters (Fig. 23.13). Here the membrane itself defines the particle size in the filtrate. Permascand has from the outset worked with GORE-TEX® membranes.

Apart from not requiring filtering aids, such as α -cellulose, membrane filters are very simple to automate, since they can be immediately brought on-line after back-pulsing. Registers that are suitable for retrofitting have been developed by Permascand and Akzo Nobel and are employed by many other plants, such as those at Bayer Uerdingen. Their operation at these plants has been successful.

In the chlorate removal system the pH may be very low. Here the material of preference is some kind of alloyed titanium. The noble alloy constituents is at the 0.05% level, which is lower than that found in the established grade 7 alloy. However, temperature and pH tolerance will be important when deciding which alloy to employ.



Fig. 23.12 A filter frame.

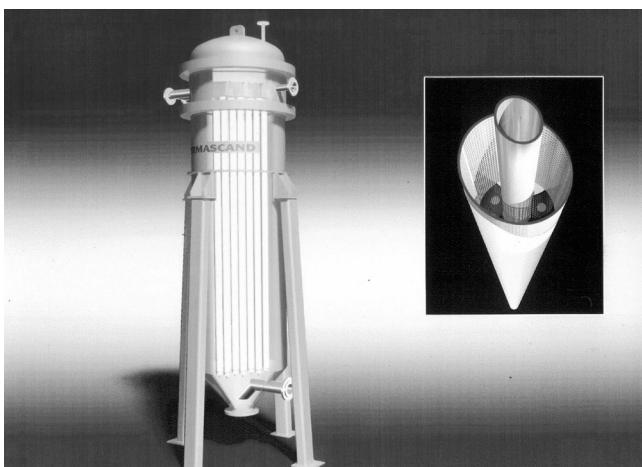


Fig. 23.13 Membrane filter and cartridge.

Other typical uses of titanium in a membrane cell process are in the pipelines for hot anolyte and in the anolyte collecting tanks as well as dechlorination systems that normally work under vacuum and sometimes limit the use of loose linings.

23.4.2 The diaphragm process

Unlike in the other two electrolysis processes, the brine is not recirculated and the temperature in the system can be chosen according to optimum conditions and therefore comparatively little titanium is used in a diaphragm cellroom. However, there are some clear candidates. An example is the cell blanket where Permascand has a newly patented design comprising bellows welded to the anode collar. The chlorine header and also the cell top are other components that could be manufactured from

titanium. The combination of high-temperature chlorine and FRP materials cannot be sustained by all end-users, however, and legislation makes the use of such consumable materials more and more expensive. Thus, there may be openings for using titanium alloys.

23.4.3 The mercury process

As every operator of a mercury cellroom knows, corrosion of rubber-lined parts of the cell is a general occurrence. The softer the rubber, the higher the speed of corrosion.

One product that has been developed for mercury cells is a loose liner (Fig. 23.14), which is fitted on-site in the anode workshop and fastened with titanium nuts (Fig. 23.15). The riser tube is tightened using a Bakelite® pressure plate.



Fig. 23.14 Loose liner for amalgam cells.

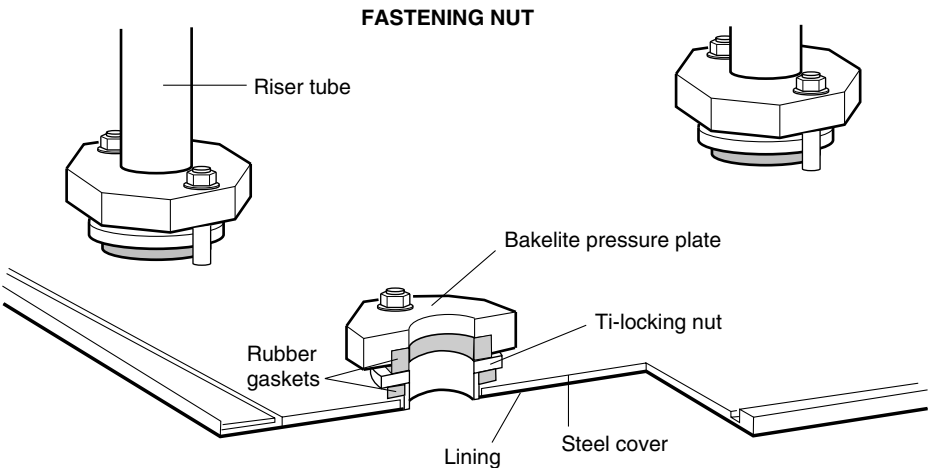


Fig. 23.15 Cross-section of a fastening nut.

The titanium lining can actually be placed on top of an existing rubber lining, which must be cleaned using high-pressure water or similar method, or it can be applied directly to the steel casing. In the latter situation, some precautions have to be taken to avoid brine condensates flowing into the void between the steel cover and the titanium lining.

In order to handle hot chlorine gas from the cells a header system has been developed (Fig. 23.16) whereby stray current dumpers take care of the brine condensates that would otherwise result in damage.



Fig. 23.16 Chlorine header of an amalgam cell.

23.4.4 Miscellaneous applications

Other uses of titanium are in the construction of anolyte pipes, anolyte tanks, and dissolver and maturing tanks in the brine system. Here pure titanium cannot always be justified and instead rubber linings or polymeric materials are also used. Where the demand on uptime is rigorous, titanium-lined steel may be considered instead of rubber.

In Sweden where demand exists for huge hypochlorite tanks, a new lining technique has been developed. The technique is applied to large reaction tanks, manufactured with capacities of 100–150 m³. The lining utilises titanium alloy.

Another potential material for cell construction purposes is nickel. For instance, Eka Chemicals has employed nickel cartridges with standard GORE-TEX® membranes to remove graphite particles directly from a caustic decomposer. The result was promising. Not only was the graphite removed but the quantities of mercury were reduced to levels of <10 µg. Aside from the cleaner caustic, the volume of sludge was drastically reduced since no pre-coat was required in this procedure.

23.5 Conclusion

Returning to the main theme – cost – money is the driving force behind much capital investment. In this chapter a summary of the economics behind the use of titanium has been provided. The savings indicated were based on interviews with end-users.

This chapter has shown many examples where the use of titanium substitutes or titanium original parts is justified financially. Although occasionally more expensive, paying a premium initially can be justified especially when titanium is involved. Quality of the product remains long after the price is forgotten!

Chapter 24

Brine Purification by Ion Exchange with Water Elution

C J Brown, M Sheedy, A Russer and W K Munns

24.1 Introduction

The susceptibility of chlor-alkali cell performance to brine purity is well known and some means of maintaining brine purity is essential. Two of the major impurities of concern are hardness (e.g. calcium and magnesium) and sulphate. In the simplest case, the brine purification 'system' may be a simple purge of depleted brine from the circuit to sewer. This is becoming unacceptable, however, owing to the value of the salt, as well as environmental restrictions. Precipitation techniques based upon calcium or barium are also being used. The usual approach is the classic lime/soda softening process, which is capable of removing hardness as well as sulphate impurities. The effectiveness of calcium sulphate precipitation is limited, however. Barium sulphate precipitation through addition of barium carbonate or barium chloride is much more effective, but handling and disposal of barium salts, which are deemed hazardous, can be problematic. Due to very stringent brine hardness requirements with membrane cells, primary softening by lime/soda precipitation is supplemented by chelating ion exchangers, to obtain final hardness levels of less than 0.05 mg l^{-1} .

While existing technology is capable of meeting brine purity requirements, there seems to be a significant level of interest in new brine purification technology which can address one or more of the limitations of the prior art. The alternatives for purification of salt are limited to a large extent by economics. It is difficult to justify the use of significant amounts of energy or even inexpensive chemicals such as acid and caustic to purify a cheap commodity such as salt. Alternative salt purification processes that do not consume chemicals or energy and do not generate solid waste would be very attractive.

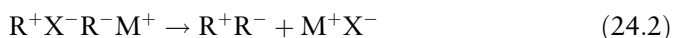
24.2 The Recoflo™ water elution ion-exchange process

24.2.1 Amphoteric ion-exchange resins

A family of novel ion-exchange resins has been developed for separating different types of salts. Unlike conventional ion-exchange resins which are either cation or anion exchangers, these resins are amphoteric. Each resin bead has *both* cation and anion exchange groups. Although the mechanism is not fully understood, for discussion purposes, the freshly regenerated resin can be considered to be in the 'self-neutralised' form (R^+R^-), i.e. the anion exchanger bearing a positive charge, R^+ , is neutralised by a cation exchanger bearing a negative charge, R^- . During the service or uptake cycle, the cation and anion associated with the impurity (e.g. M^+X^-) are taken up by the resin together. This is depicted in Equation 24.1:



When the resin makes contact with water, it becomes less selective for the salt impurity and the resin self-neutralises, again liberating the salt impurity (see Equation 24.2):



The anion and cation exchange functional groups on the resin are chosen to have high affinity for the salt impurity to be removed (i.e. MX) and a low affinity for the salt product to be left behind. A different resin is generally required for each separation. The exact composition of the resins is proprietary; the basic process, however, is the same for each.

24.2.2 The Recoflo™ ion-exchange process

In 1963 a new process for separation of strong acids from metal salts was introduced [1]. Called *acid retardation*, the process is different from conventional ion exchange in that regeneration is achieved with only water – no regenerant chemicals are required. Consequently, economical recovery of a chemical as cheap as sulphuric acid can be considered. Although a few early attempts were made to exploit the acid retardation process commercially, it was not until 1977, when a system called the APU® (acid purification unit) was developed, that the process became commercially viable. Since that time, the metals industry has embraced the technology, with almost 1000 APUs having been installed in over 40 different countries on applications such as purification of sulphuric acid anodising baths [2] and nitric/hydrofluoric stainless steel pickle liquors [3, 4].

One of the reasons that it took so long for the acid retardation process to become

commercialised is that conventional ion-exchange designs, originally developed for treatment of large volumes of water, are not well suited to the treatment of small volumes of concentrated solutions. As with the APU, the new brine purification systems take advantage of an ion-exchange technique called RecofloTM, which utilises short resin beds (7.5–60 cm), fine resin particles (75–150 μm) and countercurrent regeneration. The RecofloTM column contains no freeboard, thus avoiding one major cause of dilution. Fine-mesh resins allow the use of very high flow rates, thereby helping to reduce equipment size and capital cost. Fine resins also tend to reduce axial dispersion of fluid in the column, further reducing dilution and intermixing. A number of patented innovations [5], which were introduced in 1985 to improve flow distribution, further enhanced the performance of the RecofloTM process, making it ideal for the treatment of concentrated brines.

There is indeed a striking similarity between the salt separation processes discussed here and the acid retardation process. Consequently, it was possible to use the same basic process flow-sheet and equipment for these salt purification processes that have been extensively used for over 20 years for APU systems.

24.2.3 Basic operation and equipment design

There are two steps in the basic process: the ‘upstroke’ and the ‘downstroke’ (see Fig. 24.1). During the upstroke, feed brine solution bearing impure salt is pumped into the bottom of the ion-exchange resin bed. The impurity (MX) is sorbed by the resin particles according to Equation 24.1 and a purified brine solution is collected from the top of the bed. Next, during the downstroke, water is pumped into the top of the bed, desorbing the brine impurity from the resin according to Equation 24.2 so that a solution of the brine impurity is collected from the bottom of the bed. The total cycle typically takes about 2–10 min to complete and repeats successively.

The resin bed is typically 30 cm (12 in.) in height. Scale-up is accomplished by increasing the bed diameter. The systems can be assembled into compact, skid-mounted units, which can be fully tested prior to shipment. This minimises installation and start-up costs. Typical units range from small ‘off-the-shelf’ units with 15 cm (6 in.) diameter beds, which process 20–200 l h⁻¹ of feed solution (depending on the application), to large custom units equipped with beds up to 274 cm (108 in.) in diameter (see Fig 24.2), which process more than 300 times as much. For still larger applications, multiple units are installed in parallel.

A consideration in the design of a Recoflo system is adequate pre-filtration of the feed solution. The fine resin beds employed in the system will plug-up with any suspended material that is not filtered out prior to treatment. This is not a major issue for chlor-alkali brines, however, which are relatively clean. Disposable polypropylene cartridge filters should suffice in most cases.

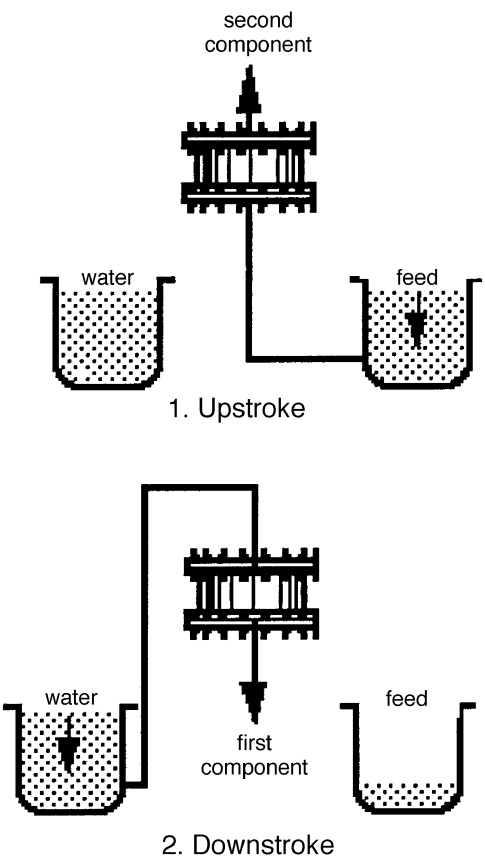


Fig. 24.1 Recoflo™ water elution operating cycle.

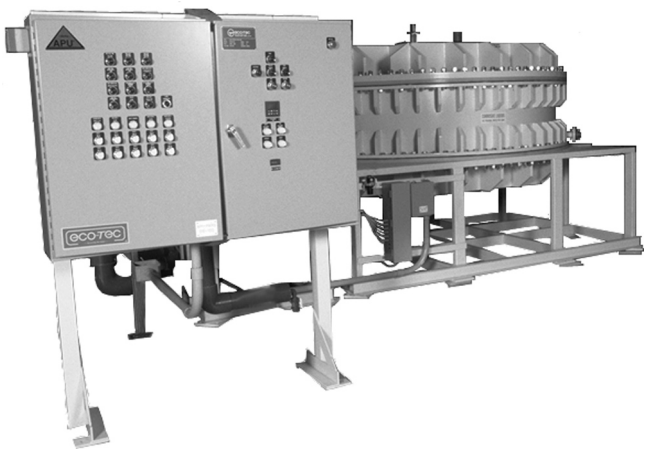


Fig. 24.2 Large Recoflo™ unit with 274 cm (108 in.) diameter resin bed.

24.3 Sulphate removal

24.3.1 Other ion-exchange processes

Ion-exchange processes employing weak base resins have been previously proposed for removal of sulphate contamination from brine [6]. In this earlier process the brine is diluted to about $100\text{--}150\text{ g l}^{-1}$ before treatment. After loading it is regenerated with saturated brine. Given that significant quantities of sodium chloride ‘regenerant’ are consumed to recover the original sodium chloride brine, it is not too surprising that this approach has not been widely adopted by the industry. In addition, provision to remove the excess dilution water may be necessary.

A process that employs a powdered inorganic ion exchanger in a slurry has also been proposed [7]. This process appears rather cumbersome and messy since the ion-exchange materials must be repeatedly filtered and re-pulped over each cycle. This process will also be expensive to operate, since the ion exchanger must be regenerated with NaOH.

Another ion-exchange system has recently been developed by Nippon Rensui [8]. The Nippon Rensui system employs an amphoteric ion-exchange resin called Diaion DSR01 which can be eluted with water. In the DSR01 system, the resin takes up the sodium chloride and ‘rejects’ the sodium sulphate. Purified NaCl is then recovered from the resin by water elution. This seems like a difficult approach since it is necessary to take-up huge amounts of NaCl on the resin in order to separate out a relatively small amount of sulphate impurity. Excessive dilution of the purified brine may also be an issue with this process.

24.3.2 The BDS system

The Eco-Tec ‘BDS’ (brine de-sulphurisation system) process uses a very different type of amphoteric ion-exchange resin. Unlike the DSR01 process, the BDS resin takes up the dilute sodium sulphate impurity and the concentrated, purified NaCl passes through the bed and is collected as product. The sodium sulphate impurity is then eluted from the resin with water. There is a fundamental advantage with this approach in that the amount of salt which must be adsorbed by the resin is lower by a factor of about 30 times. This reduces appreciably the amount of resin required and the associated equipment and cost. Typical BDS results are shown in Table 24.1.

It should be noted that the operating parameters of the unit can be adjusted to suit the client’s needs. These particular operating conditions were an attempt to maximise productivity (i.e. minimise capital cost) and minimise the waste volume. While the NaCl recovery efficiency is about 96%, the brine purity is not exceptionally good (43.4% sulphate removal). This is not considered a disadvantage, however, since the low removal efficiency can be compensated for by increasing the flow of feed that is treated by the system. If necessary, removal efficiencies of over 95% can be obtained.

Table 24.1 Typical BDS sulphate removal results.

	Relative volume (l l ⁻¹ feed)	[Na ₂ SO ₄] (g l ⁻¹)	[NaCl] (g l ⁻¹)
Feed	1	6.00	203
Waste	0.381	6.82	21.3
Purified salt	1.11	3.06	174
Removal/loss	—	43.4%	4%
Mass balance	—	0.1%	— 1%

Although the process is actually somewhat more effective in treating saturated brine, a typical flow-sheet would probably locate the BDS system so that depleted brine from the cells would be treated.

Although the BDS resin is very stable, as with all ion-exchange resins, it is susceptible to oxidation by chlorine. For this reason, any residual chlorine in the brine after vacuum dechlorination should be reduced prior to BDS treatment. This is typically done with sodium bisulphite. The small additional sulphate load that results can easily be handled by the BDS system.

The BDS system is capable of processing brine with much higher sulphate concentrations. In one case, a source of waste brine bearing high sulphates was available at no cost. The only problem was finding an economical way to lower the sulphate level. Since the brine was free, maximisation of NaCl recovery efficiency was not a priority. As discussed above, operating conditions of the process may be varied to optimise capital cost, brine recovery efficiency or purity levels, as required. Typical data at higher sulphate levels are shown in Table 24.2.

Table 24.2 Typical BDS sulphate removal results: high sulphate level.

	Relative volume (l l ⁻¹ feed)	[Na ₂ SO ₄] (g l ⁻¹)	[NaCl] (g l ⁻¹)
Feed	1	20.1	303
Waste	1.53	10.55	22.4
Purified salt	1	3.96	272
Removal	—	79.9%	11.3%
Mass balance	—	0.3%	2.8%

It should also be noted that the BDS system has also been successfully tested on potassium brines.

24.3.3 BDS economics

A comparison is made in Table 24.3 between the operating costs of BDS and two alternatives: barium treatment and the DSR01 ion-exchange process.

Barium treatment is generally preferred to purging where salt discharge to the sea is not an option. The barium cost in Table 24.3 allows for carbonate credits.

While the DSR01 ion-exchange system appears to be reasonably efficient, resin cost with that system is a major maintenance cost item. The BDS system uses up to 95%

Table 24.3 BDS operating cost comparison (\$'000)^a.

	Barium treatment	DSR01 [8]	BDS
Salt loss	—	14	47
Water usage	—	47	62
Barium cost	825	0	0
Sludge removal	140	0	0
Energy	0	25	7
Maintenance	0	144	14
Total cost	965	230	130

^a Basis: 8400 h operation per year; 100 kg h⁻¹ sodium sulphate removal; brine contains 215 g l⁻¹ NaCl and 9 g l⁻¹ Na₂SO₄.

less resin than the DSR01 system. In addition, with DSR01, the brine may be cooled significantly during treatment.

BDS systems consume slightly more water and lose more salt than the other systems. This is offset by low energy and maintenance costs. The BDS system offers annual savings of US\$835 000 versus barium treatment. It is also significantly less expensive to operate than the DSR01 process, largely owing to the higher resin replacement cost of the latter system (Table 24.3).

24.3.4 Water reuse

In many areas where chlor-alkali plants are found, water is in short supply. Even the modest water usage of the BDS system can strain the limited resources available to the plant.

To reduce the water usage of the BDS system to the lowest possible level, reverse osmosis (RO) can be used to reclaim up to 75% of the water from the BDS waste. The electrical and maintenance costs required to operate the RO system are more than balanced by the savings in water. In fact, several cases have shown that where water is in short supply, the savings can offset the additional capital cost of the reverse-osmosis system within three years.

24.4 Brine softening

24.4.1 Chelating ion-exchange brine polishers

The susceptibility of membranes to hardness fouling is well known. The development of chelating ion-exchange resins for brine softening has been a key factor in making the membrane cell viable. Chelating ion-exchange units are capable of reducing calcium levels in brines from up to 10 mg l⁻¹ to less than 20 µg l⁻¹. However, these units have a number of limitations and disadvantages.

- (1) The resins require two-stage regeneration with hydrochloric acid followed by sodium hydroxide. Although these chemicals may be locally produced, the cost

is not insignificant. The materials of construction employed for piping and column internals, which must be compatible with HCl, are expensive. Moreover, handling and storage of a corrosive and hazardous chemical such as HCl requires special consideration.

- (2) Chelating resins undergo volumetric change by as much as 50% in converting from the hydrogen form to sodium form. This tends to cause attrition of the resin and reduce its life.
- (3) The process is limited to secondary treatment or polishing applications where the amount of hardness to remove is relatively small [9].

24.4.2 The BDH system

A novel amphoteric ion-exchange process called BDH was developed by Eco-Tec in 1998 to purify brines used for regeneration of sodium-cycle ion-exchange water softeners. The particular application involved softening of oil-field-produced water containing total dissolved solids levels of more than 4000 mg l⁻¹. It was found that, providing the brine regenerant was sufficiently pure, a strong acid cation (SAC) exchanger could be employed instead of the usual weak acid cation (WAC) units which, like chelating resins, require two-stage HCl/NaOH regeneration. The BDH process provided a clean, simple, inexpensive means of purifying the brine.

The particular amphoteric resin that is employed in the BDH process has a high affinity for calcium and magnesium chloride in concentrated sodium chloride brines. In dilute solutions the selectivity is lost, so that regeneration can be effected with a simple water wash. The process was found to be effective over a wide range of hardness and brine concentrations.

Typical pilot-plant BDH results are shown in Table 24.4. The brine that was treated in this case was made up with vacuum pan salt to a concentration of approximately 10% w/w, which is the concentration employed for regeneration of the SAC ion-exchange softener unit. Included in the table is the entrained volume of feed solution (i.e. feed void) which is displaced from the bed prior to regeneration on each cycle. The feed void would normally be recycled to the feed tank and processed in subsequent cycles.

As can be seen from Table 24.4, both the calcium and magnesium contaminants

Table 24.4 BDH brine softening results: dilute vacuum pan salt.

	Relative volume	[Ca] (mg l ⁻¹)	[Mg] (mg l ⁻¹)	[NaCl] (g l ⁻¹)
Feed	1	37.25	0.80	103
Purified brine	0.966	0.0	0.00	97.9
Feed void	0.0808	36.0	0.80	71.2
Waste	0.417	81	1.7	0.8
Removal	—	99.9+%	99.9+%	0.4%
Mass balance	—	-2%	-3%	-1%

were removed down to below the limits of detection employed ($\text{Ca} = 0.1 \text{ mg l}^{-1}$, $\text{Mg} = 0.01 \text{ mg l}^{-1}$). This indicates the high removal capability of the process, although the purity produced under these conditions may be higher than required for the intended use. Alternative conditions have been developed which would provide higher productivity (i.e. lower capital cost) at somewhat lower removal efficiency.

Table 24.5 shows the results obtained in treating a saturated solution of vacuum pan salt which would be more typical of that required for primary treatment in the chlor-alkali industry. Note that the higher feed concentration did not adversely affect the removal efficiency, even considering the higher hardness concentration. Complete hardness removal was obtained with 99% recovery of the NaCl values.

Table 24.5 BDH brine softening results: saturated vacuum pan salt.

	Relative volume	[Ca] (mg l^{-1})	[Mg] (mg l^{-1})	[NaCl] (g l^{-1})
Feed	1	106	2.00	292
Purified brine	0.968	0.0	0.00	288
Feed void	0.0775	326	6.70	210
Waste	0.382	203	3.9	7.1
Removal	—	99.9+%	99.9+%	1.0%
Mass balance	—	−3%	0%	1%

It is not known whether this process would be competitive with the lime/soda precipitation process for primary treatment. For new plants, the main issue is capital cost. The lime/soda process is relatively inexpensive for large-scale plants. For small plants, the BDH system may be competitive, particularly for packaged turn-key plants, if installation and start-up costs are taken into consideration. The BDH system is very compact and can be quickly started and easily operated with minimal labour requirements.

The above results indicate that the process may even be capable of matching the final purity currently offered by chelating polishing units. Although BDH may overcome a number of the disadvantages of the chelating process, one potential disadvantage of the BDH system is the relatively large volume of waste water produced from the water elution. This issue is currently being addressed.

24.5 Conclusion

Novel ion-exchange technology has recently been developed for purification of brine. Different resins have been developed for removal of sulphate impurities as well as calcium and magnesium hardness. The process is very simple and since only water is consumed to regenerate the ion-exchange resins, the operating costs are extremely low. The equipment, which is similar to that currently widely utilised for purification of waste acid, is very compact. It is expected that commercial-scale systems of both types will be installed later in 2000.

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Chapter 25

Emission of Chlorine Dioxide in a Hypochlorite Production Unit in the Steady State and at Peak Load

I J Pek

25.1 Introduction

In the electrolysis plant of Akzo Nobel in Rotterdam a hypochlorite production unit is in operation. This unit has two functions: handling chlorine-containing waste gases from the plant and production of hypochlorite. The reaction is carried out in a two-step apparatus in which a liquid jet-loop reactor and a packed column are in series. In this way chlorine is converted to hypochlorite and emissions of chlorine to the atmosphere are avoided.

It was found that the concentration of total oxidants measured in the off-gas from the hypo unit varied with process conditions. Precise analysis of the off-gas showed that under certain conditions chlorine dioxide is formed in the reaction step where the hypochlorite concentration is approximately $160\text{--}180\text{ g l}^{-1}$. In the sections below formation of chlorine dioxide in the hypochlorite unit is discussed with regard to process conditions and peak load of the feed stream. In essence, the emission of chlorine dioxide can be reduced to nearly zero by using a scrubber in which the chlorine dioxide reacts with hydrogen peroxide.

25.2 The hypochlorite production unit

Production of hypochlorite takes place in a two-step absorption unit in which 23% caustic solution is fed counter-currently to the chlorine feed-stream. In the first step – the liquid jet-loop reactor – about 90% of the chlorine is converted to hypochlorite. In step two – a packed column – a very efficient absorption [1–3] is carried out in which the chlorine concentration in the off-gas is reduced to $<1\text{ ppm}$. The operating window of this apparatus with respect to chlorine load is quite large and varies from 100 to 6000 kg h^{-1} of chlorine. This high capacity is necessary for the consumption of peak loads from the electrolysis plant during short time periods. During start-up or shut-down of one electrolyser the total chlorine peak load can vary from 100 to 300 kg in just a few minutes.

The hypochlorite produced has an active chlorine concentration of $160\text{--}180\text{ g l}^{-1}$ and a free caustic concentration of $4\text{--}8\text{ g l}^{-1}$. Figure 25.1 illustrates the simplified layout of the two-step chlorine destruction unit. All measurements are carried out under steady-state conditions under different peak loads of chlorine.

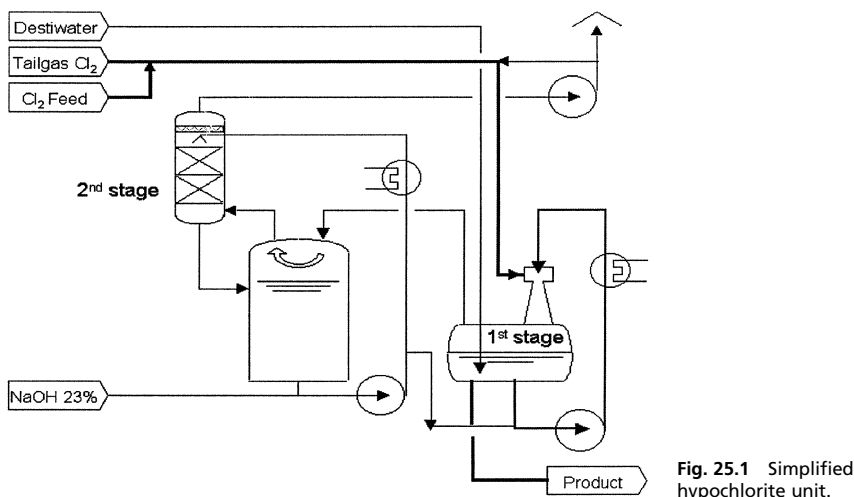


Fig. 25.1 Simplified hypochlorite unit.

In the first step the chlorine from the tail gas and chlorine feed reacts with the caustic in the jet-loop reactor. The advantage of the jet-loop reactor is that it also acts as a suction device for the gas stream. The residence time of the liquid in step one is dependent on the capacity of the hypochlorite production and liquid level in the tank and varies between 1 and 4 h. A heat exchanger in the loop controls the temperatures in steps one and two. The amount of caustic in the feed-tank of step two is the back-up for failure of chlorine liquefaction.

The inert flow in the system is about $5000\text{ m}^3\text{ h}^{-1}$. Taking into account the flow of liquid in step one, the gas-liquid ratio is about 35 which is far from normal for jet-loop reactors as such reactors normally operate at a gas-liquid ratio of 0.5–3 [4].

25.3 Chlorine dioxide emission

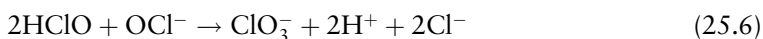
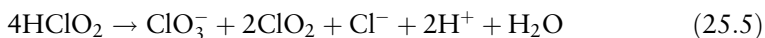
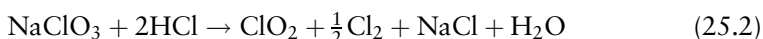
When the reaction temperature of step one increases, the total oxidant concentration in the off-gas is $>6\text{ mg m}^{-3}$, but this depends on capacity and hypochlorite concentration. Careful analysis with infrared methods demonstrated that this total oxidant concentration was derived from chlorine dioxide. Measurements of the concentrations between steps one and two showed that concentrations were higher than in the off-gas and that hypochlorous acid (HOCl) was also found, which was totally absent in the off-gas.

Also observed were peak emissions of total oxidant of $>20 \text{ mg m}^{-3}$. This led to odour complaints. It is known that short-term exposure can lead to irritation of the eyes, nose, throat and skin with headache and vomiting symptoms. Chronic exposure to chlorine dioxide can lead to chronic bronchitis and emphysema.

The exposure limits of chlorine dioxide are rather low: the MAC value is 0.3 mg m^{-3} and the NER (Dutch guideline) value is 1.0 mg m^{-3} .

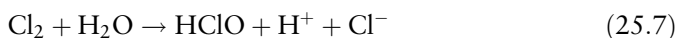
25.4 Formation of chlorine dioxide

Several reactions are possible in the formation of chlorine dioxide [5] and in reality a group of reactions and species interactions take place in the hypochlorite solution. Usual reaction components are NaOCl, HOCl, HCl, Cl^- , HClO_2 , NaClO_3 , ClO_2 , NaCl, H_2O , etc. In understanding the model presented in this chapter, a few of the reactions are presented below:

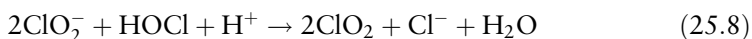


Reaction velocities and reaction equilibria are dependent on the temperature and pH at which the reaction is conducted and also the concentrations of the species involved [6–8].

A reaction scheme derived from the above reactions describes the formation of chlorine dioxide in the present production unit. Equations 25.3 and 25.4 are the key items in this scheme. In Equation 25.3, chlorite in the solution reacts with chlorine to form chlorine dioxide. With the water–chlorine equilibrium



the reaction of Equation 25.3 can easily be converted to:



The above reaction has been previously described [9] where the influence of the chloride ion is measured. It turns out that chloride concentration also has an effect on the reaction rate. The reaction rate can be described by:

$$\frac{d[\text{ClO}_2]}{dt} = \{k_1 + k_2[\text{Cl}^-]\} [\text{ClO}_2^-] [\text{HOCl}] [\text{H}^+] \quad (25.9)$$

In the production unit for hypochlorite the concentration of chloride is nearly constant, but concentrations of HOCl and H^+ strongly depend on the local pH of the solution.

Chlorine dioxide can be formed out of the chlorite by either of the reactions described by Equation 25.3 or 25.8. Equation 25.1 describes the chlorite formation. The chlorine concentration in the liquid is normally very low as the reaction with caustic (Equation 25.4) is very fast. The concentration of chlorine and/or hypochlorous acid HOCl can increase on depletion of hydroxide ions in the liquid. As in step two of the hypochlorite unit, the caustic concentration is in the order of $4\text{--}10 \text{ g l}^{-1}$ and it is possible to conclude that at the gas-liquid interface the concentration might be quite low owing to the fast reaction with chlorine.

Infrared spectroscopic measurements of the gas travelling between steps 1 and 2 of the unit show that the HOCl is absorbed completely in step two. However, the chlorine dioxide that is formed in step one is hardly absorbed at all in step two with most being stripped from the gas owing to its low solubility and high flow rate.

Measurements taken in the plant show that the formation of chlorine dioxide is dependent on temperature, production capacity, hypochlorite concentration, caustic concentration and residence time of the hypochlorite in the reactor at step one.

For the steady-state situation, chlorine dioxide emissions are measured when altering process variables such as concentration, temperature and production capacity. These measurements result in a number of relationships, plotted in Figs 25.2 and 25.3, with respect to the hypochlorite installation.

Figure 25.2 shows that the emission of chlorine dioxide strongly increases with increasing temperature and is linear with increasing production capacity under the steady-state condition. In Fig. 25.3 it is seen that emission increases with increasing

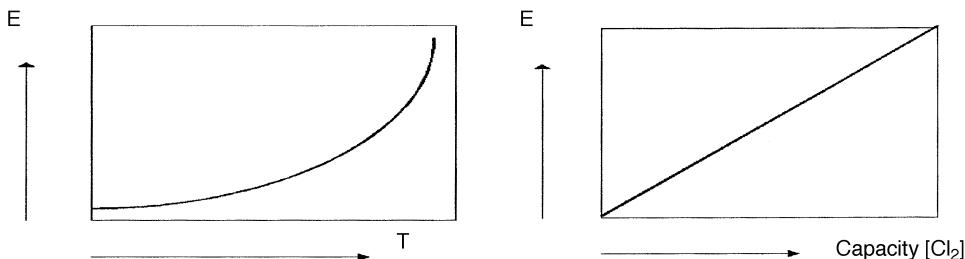


Fig. 25.2 Emission of chlorine dioxide as a function of temperature and capacity.

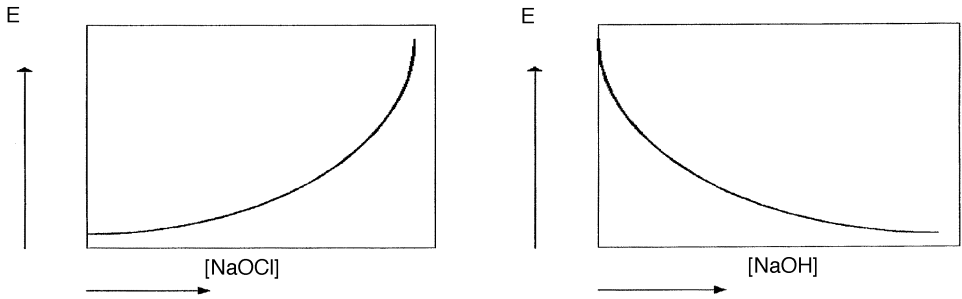


Fig. 25.3 Emission of chlorine dioxide as a function of NaOCl concentration and free caustic concentration.

concentration of sodium hypochlorite and that the emission decreases with increasing concentration of free caustic. When holding the liquid in the reactor of step one to increase the residence time, emission also increases (not shown).

In the non-steady-state situation, i.e. when the chlorine supply is at peak load, a peak in the emission of chlorine dioxide is also measured. The measurements in this situation are presented in Fig. 25.4. Measurements were performed at time intervals and the symbols on the plots reflect the average concentration at a particular time interval.

The time elapsed between the start of the peak in the chlorine feed and the increase of the chlorine dioxide emission is about 2 min. The height of the peak is dependent on the reaction temperature, hypochlorite concentration, production capacity, gas

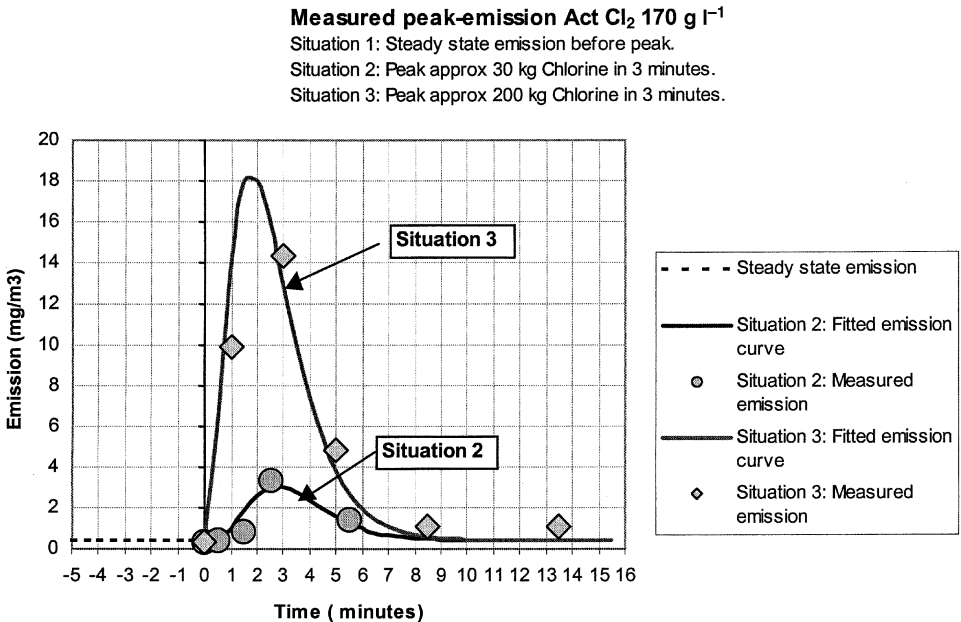


Fig. 25.4 Emission during peak load, 170 g Cl₂ per litre.

mixing, residence time, etc. The emission peaks shown in Fig. 25.4 were obtained with two chlorine peak loadings in the feed-stream: situation 1 with 30 kg of chlorine in 3 min; situation 2 with 200 kg of chlorine. During the 3 min peak period, these values translate into chlorine flow rates of about 600 and 4000 kg h⁻¹, respectively. The active chlorine concentration for both situations was 170 g l⁻¹ at a temperature of 14°C. As is shown in Fig. 25.4 the emission of ClO₂ from the larger chlorine feed is much greater than the emission from the smaller feed. In practice the redox measurement determines the quantity of caustic to be dosed.

Larger production capacities result in greater ClO₂ emissions. The initial emission value is reached around 15 min after the peak value has occurred. The measured values displayed in Fig. 25.4 are plotted with a Poisson fit meaning that a pulse disturbance can be simulated by production tanks in series. For the highest emission peak it is found that the best fit is obtained with ideally three stirred tank reactors; the lower peak is smoother and five tanks in series give the best fit.

Figure 25.5 plots the results of the same experiments with a lower active chlorine concentration. Compared to the 170 g l⁻¹ of hypochlorite solution, the emission peaks here are lower with a 30% reduction. The same effect is seen with the steady-state emission experiments, with a higher hypochlorite concentration giving higher emission values under the same process conditions.

A further experiment was performed with an extremely high caustic concentration of 38 g l⁻¹ and an active chlorine concentration of 160 g l⁻¹. The results are shown in

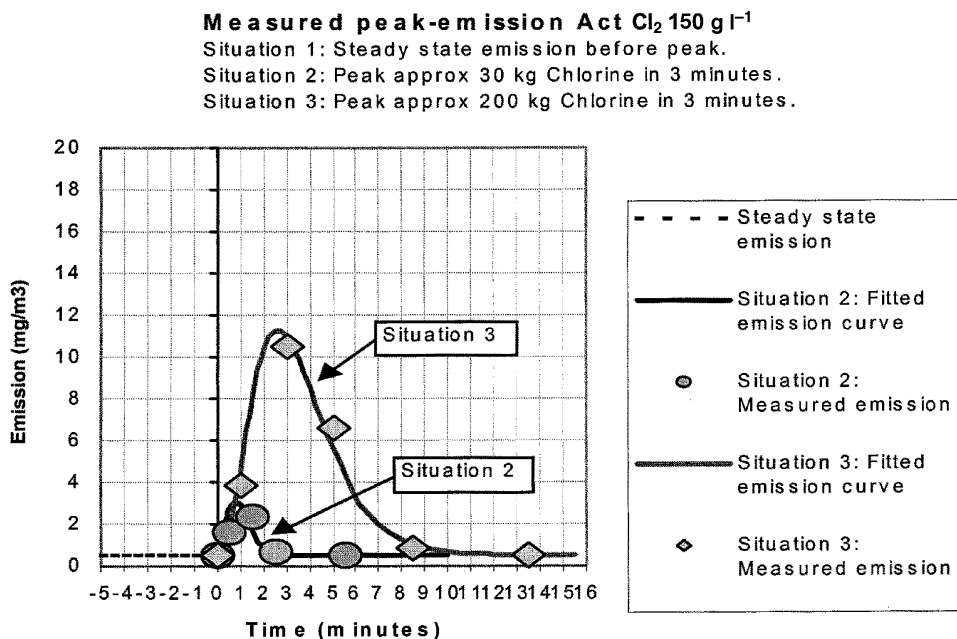


Fig. 25.5 Emission during peak load, 150 g Cl₂ per litre.

Fig. 25.6. A free caustic concentration increased to 38 g l^{-1} constitutes a level that is about 32 g l^{-1} higher than normal and the ClO_2 emission peak reduces by about a factor of four; however, there is still a peak. In the measurements completed in this section no relationship was found between ClO_2 emission and chlorate concentration in the hypochlorite solution.

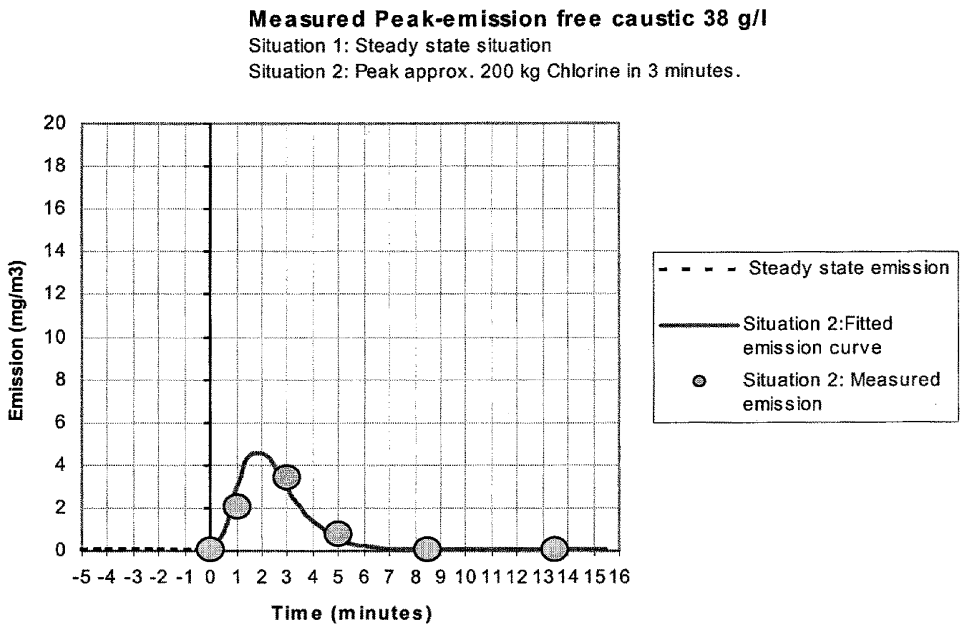


Fig. 25.6 Peak emission with high concentration of free caustic.

25.5 Modelling

The effects of the steady-state situation and the effect of the peak load can be described using a model. When the caustic concentration is low, either through initial concentration effects or by mass transfer limitations, the reaction of chlorine with chlorite can occur and chlorine dioxide (Equations 25.3 and 25.8) is formed near the gas-liquid interface. The concentration of chlorite seems quite important and is influenced by temperature (decomposition) and the hypochlorite concentration. A higher chlorite concentration will give, according to the reactions of Equations 25.3 and 25.8, a higher chlorine dioxide content in the presence of chlorine and/or hypochlorous acid.

The total quantities of chlorine dioxide formed are quite low and are in the order of 0.5–3 g for the peak-load experiments. Because this is a relatively low range of values, it is not easy to discover any correlations with other species involved in the reactions as the concentration may hardly change. This could also be one of the reasons that there is no relationship found between chlorate and the ClO_2 emission values.

From the steady-state experiments, an equation can be derived for the ClO_2 emission (E) involving the following parameters: temperature (T), hypochlorite concentration (C), production capacity (P) and liquid level of the reactor (L_{V751}):

$$E = C_0 P (C/155)^4 \cdot L_{V751} \cdot F(T)$$

where

$$F(T) = 0.8563 - 0.142T + 0.0251T^2 - 0.00155T^3 + 0.0000348T^4$$

The emission is very strongly dependent on the temperature. At 30°C the emission is about eight times the emission at 10°C. The reason for this strong dependency is not quite understood. The reaction of chlorine with caustic is enhanced, however, and this will result in lower caustic concentrations and also lower chlorine concentrations. The quantities of by-products formed, such as chlorite, will become higher as well as the amounts of decomposition products. Solubility in the liquid phase will decrease on increasing temperature but cannot account for the large variations in emission.

Increasing the free caustic concentration gives higher concentrations at the gas-liquid interface and lower emissions in both the steady-state and peak-load situations.

When the capacity is increased under the same process conditions the caustic concentration is increased on higher dosing. As the quantity of free caustic in the end-product and in the liquid flow of the jet-loop reactor is the same, the percentage of caustic reacting with chlorine increases by roughly 25–60% when the production capacity is increased. Depletion of caustic at the liquid–gas interface can then occur more easily.

Increasing the liquid level in the reactor at step one gives a longer residence time and this probably increases the precursor concentration of chlorite. The same reason is assumed for increasing the hypochlorite concentration which leads to higher concentrations of by-products in the hypochlorite solution. Formation of hypochlorous acid, for example, results from depletion of caustic [2].

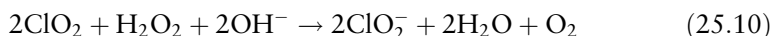
When there is a peak flow of chlorine in the feed-stream the redox potential decreases and the amount of caustic that is dosed increases automatically. Caustic is fed to the jet-loop and its flow is regulated by the measurement of the redox potential. When the lead time is long there is a shortage of caustic, which results in a lower level of free caustic that leads to a higher chlorine concentration. This chlorine subsequently reacts with the chlorite in the hypochlorite solution to form chlorine dioxide. The absorption of chlorine dioxide by the caustic is then very limited in step one and is hardly absorbed at all in the caustic present in step two of the production and is emitted with the inert gas stream.

25.6 Solutions for chlorine dioxide emissions

To reduce the emission of chlorine dioxide to a regulatory level of 0.3 mg m^{-3} , several options are available. The two principal options in this quest are to change the process conditions and to install a scrubber to absorb the chlorine dioxide.

The first option might include altering the reaction temperature, caustic concentration, hypochlorite concentration, avoiding peak flow of chlorine, or faster control loops. Absorption with increased levels of free caustic is also possible with the introduction of a third absorption step where the product with a free caustic concentration of about $50\text{--}100 \text{ g l}^{-1}$ is converted to an end-product with a concentration of $4\text{--}8 \text{ g l}^{-1}$ free caustic. Decreasing the reaction temperature is also possible, but it is costly especially during summer when cool-water temperature prices are higher. Peaks in the chlorine feed cannot be avoided as the installation also functions as a unit to handle waste streams containing chlorine. These factors taken together suggest that this is not the most economic way to solve the emission problem.

The second option involves the use of a ClO_2 scrubber. This is a technique presently used in the paper and pulp industry. In the scrubber, the chlorine dioxide reacts with another chemical, such as a sulphite, DMSO, white spirit or an alkaline hydrogen peroxide solution. The hydrogen peroxide solution is most suited to the process described in this chapter as there are no waste streams. The reaction of chlorine dioxide with the alkaline hydrogen peroxide solution is rapid [10]. The reaction equation is as follows:



The reaction products are chemicals that commonly occur in the hypochlorite solution, which is an advantage over using a sodium sulphite solution as an absorption medium, for example, as its use would entail removal of sulphuric impurities.

The chlorine dioxide emission totals following this scrubbing procedure are very low, and result from the use of low concentrations of hydrogen peroxide. The advantages are that the peak loads of chlorine can be controlled more easily and the amounts of hydrogen peroxide needed (and therefore its cost) are relatively small.

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Chapter 26

New Process Options for Hypochlorite Destruction

E H Stitt, F E Hancock and K Kelly

26.1 Introduction

The abatement of chlorine vents and the subsequent destruction of the resulting sodium hypochlorite has been the subject of many studies. There are a variety of approaches to the waste hypochlorite destruction including chemical dosing, homogeneous and slurry catalysis as well as fixed-bed catalysis. For the most part these processes treat the hypochlorite at its natural strength: the stoichiometric equivalent strength of the caustic soda fed to the scrubber.

Generally, although not exclusively, a scrubber with a recycle loop of the caustic scrubbing liquor is used; cases of ‘once-through’ scrubbing liquor operation do exist. The scrubber may be operated in batch, semi-batch or continuous mode with respect to the liquid. Process hazards exist in batch and continuous mode, the most significant of which is over-chlorination. Batch-wise operations leads to periodic high loads on the hypochlorite destruction unit. In order to even out these loads, and improve the process safety, a study of alternative treatment options has been undertaken.

26.2 Chlorine vent abatement

In the chlorine-manufacturing and chlorine-using industry sectors, vent and purge streams containing gaseous chlorine have to be processed to avoid the emission of chlorine gas. Typical sources of chlorine-containing vent gases are tail gas from chlorine manufacturing plant, reactor bleeds, reactor off-gases from chlorinated hydrocarbon oxidation, blow-down during chlorine tanker operations and the pressure-relief stream in all chlorine manufacturing and application plants. These streams can be relatively time independent in the case of tail gas or purge streams, or in an unsteady state in the case of blow-down and pressure-relief incidents.

This chlorine containment is commonly achieved through scrubbing with an

alkaline solution, normally sodium hydroxide at concentrations up to 20 wt%, resulting in the generation of a sodium hypochlorite stream of up to 15 wt% through the following aqueous phase reaction:



Thus a spent scrubbing solution is obtained that contains equimolar quantities of NaOCl and NaCl. The chlorine-containing vent streams may contain also and variously CO₂, HCl and other components naturally occurring in atmospheric streams. Clearly the CO₂ and HCl have the potential to reduce the capacity of the caustic stream for chlorine removal.

A wide variety of designs and operating procedures exist in the chlor-alkali industry. These vary from once-through to recycle operation with the caustic solution, from continuous to batch addition of the caustic make-up as well as in the means of provision of a back-up reservoir of caustic for containment of chlorine-laden pressure relief and emergency shutdown streams.

- (1) A scrubber has a closed-loop recycle of caustic. The make-up caustic solution is added continuously on an ORP (oxidation–reduction potential) controller. The caustic concentration will typically be 20 wt% and thus the blow-down stream will contain approximately 15 wt% hypochlorite. Such a system will typically be provided with a large reservoir of caustic that is released on a once-through basis for containment of emergency relief streams or operated with a permanent excess of caustic, resulting in a hypochlorite concentration in the blow-down stream in the range of 6–12 wt%.
- (2) Two towers operate continuously in series at a steady state. The first, smaller, column treats the steady vents (e.g. tail gas) while the second, larger tower is designed to cope with emergency relief streams. The fresh caustic is fed to the downstream tower and the smaller tower make-up and blow-down are controlled by ORP measurement. The smaller tower operates at near exhaustion of chlorine while the second contains virtually fresh caustic. This system is ideally suited to the production of saleable, 15 wt% hypochlorite.
- (3) A scrubber fed with a continuous stream of moderate concentration caustic (1–5 wt%) without caustic recycle. The continuous stream is sufficient to abate pressure relief and emergency shutdown streams in addition to continuous treatment of normal tail gas
- (4) A scrubber with recycle where part of the caustic inventory is periodically pumped from the reservoir and replaced with fresh, 20 wt% caustic. This will be referred to as a semi-batch operation. The operating periodicity may be in the order of hours or days

- (5) A pair of scrubbers operated alternately. In the normal configuration the scrubbers are operated in series. As the caustic in the upstream scrubber becomes depleted it is taken off line and the remaining scrubber becomes the prime tower. The off-line scrubber has the hypochlorite-laden inventory discharged to be replaced with fresh caustic, and is then brought back online as the downstream tower. This will be referred to as batch operation. The minimum changeover frequency in normal operation is probably less than a day.

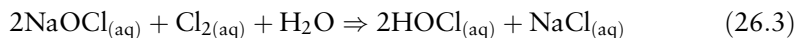
Each of these design and operating regimes places a very different demand on any hypochlorite destruction facility, from continuous treatment of high-volume low-level streams, through low flow–high concentration streams to the handling of periodically high concentration batches of hypochlorite.

26.2.1 Alternative hypochlorite reactions

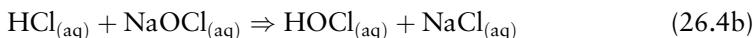
At high concentrations of hypochlorite, and temperatures sufficiently high to favour the kinetics ($>50^{\circ}\text{C}$), hypochlorite decomposes to form chlorates:



This is the reaction by which sodium chlorate is manufactured commercially. In the present context, however, the formation of chlorates is generally undesirable since they tend to be explosive and toxic. The reaction given by Equation 26.2 is strongly affected by pH and temperature as well as the hypochlorite ion concentration. As the alkali becomes exhausted, and the system is thus over-chlorinated, the rate of chlorate formation is greatly accelerated as the reaction becomes auto-catalysed by hypochlorous acid. The acid is formed by



and auto-catalyses the chlorate formation through the reactions



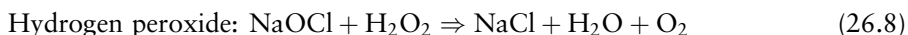
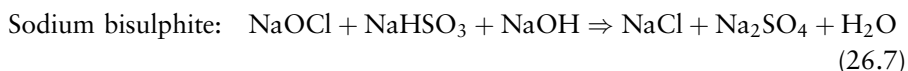
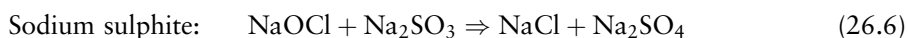
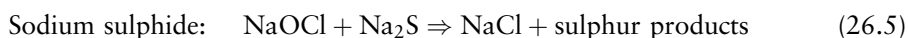
The excess of chlorine thus favours formation of HOCl which in turn accelerates the alternative route to chlorates. The reaction given by Equation 26.3 is significantly faster than that of reaction 26.1, and is strongly exothermic and thus presents run-away potential. This has been avoided historically by providing cooling within the caustic recycle or pump-around loop and by providing an excess of caustic.

26.3 Sodium hypochlorite destruction techniques

While hypochlorite in pure solutions is an industrially and commercially useful product, notably in water treatment and disinfection, incidental production exceeds demand. If discharged as a waste stream it can act as a powerful bio-toxin owing to its high oxidation potential, can form chlorinated organics when mixed with other streams and can release chlorine if the stream becomes acidic. There is thus a need to treat these waste hypochlorite streams.

The destruction of the resulting sodium hypochlorite has been the subject of many studies. There are a variety of approaches to waste hypochlorite destruction.

- (1) Chemical reduction. This is the most commonly used method of destroying hypochlorite and involves the introduction of a reducing agent to the effluent in stirred tanks. Many agents can be used, resulting in a variety of undesirable chemical end-products:



Chemical reduction can reduce the amount of free chlorine to very low levels but it is expensive for all but low hypochlorite concentrations or very low and intermittent volumes of effluent.

- (2) Thermal. Heating the solution to 60–80°C decomposes the sodium hypochlorite, albeit slowly. If the temperature is too high then this leads to the formation of chlorates via Equation 26.2. Therefore, care is required not to overheat the solution. The consequent requirement for large holding tanks and process safety issues mean that this approach is generally not favoured.
- (3) Homogeneous/slurry catalysis. The chemistry of catalytic sodium hypochlorite decomposition using transition metals was first observed in the 1830s [1]. A homogeneous batch process using Ni, Co or Cu sulphides has been in use in the chlor-alkali industry since the 1920s following further research [2, 3]. Metal slurry catalysis involves the addition of metal salts to the effluent in tanks which are either stirred or agitated via an external circulation loop. In practice, either solutions of nickel, iron and nickel, or cobalt salts are added as catalysts which form a precipitate at the high pH of the effluent.

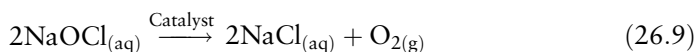
The process is dependent upon temperature, pH and hypochlorite concentration, and must be carefully controlled to avoid thermal runaway reactions. The reaction itself, combined with settling times for the catalyst slurry, can take three to four days, and the end-product – heavy metal salts – must be handled as hazardous waste.

- (4) Fixed-bed catalysis. ICI began a programme of work in late 1986 to develop an active, robust heterogeneous catalyst for hypochlorite destruction. The resulting catalyst will withstand the high pH and corrosive nature of the effluents, as well as giving a very high destruction efficiency. The result of this research was a nickel on alumina catalyst able to perform at pH 13–14 and exceed 20 000 h duration with continued high performance.

This chapter will focus on development work for the fixed-bed heterogeneously catalysed abatement process and its integration into the chlorine scrubbing process and other treatment systems

26.4 Process chemistry

The catalytic decomposition of sodium hypochlorite proceeds through the reaction:



The reaction of the aqueous solution over the heterogeneous catalyst results in the production of gaseous oxygen. A 10 wt% solution of hypochlorite produces some 30 times its volume of gaseous oxygen during decomposition. The generation of significant gas volumes during the solid–liquid reaction has a major influence on the design and operation of the reactor

The reaction is strongly exothermic, with a heat of reaction ΔH equal to 59.97 kJ mol⁻¹, which is equivalent to an adiabatic temperature rise of 1.9–2.5°C per wt% of sodium hypochlorite in the feed solution.

The catalyst used is a promoted nickel oxide on an alumina support [4], manufactured in cylindrical form. Because of the highly oxidised state of the nickel, the catalyst is resistant to classic poisons and extended lifetimes have been observed in industrial installations.

26.5 Design for total destruction

The previously published process design [5] was able to achieve total destruction of the hypochlorite down to levels of less than 100 ppm (or even <1 ppm) from a feed

concentration of 1–10 wt%. This entails conversions in the order of 99.99% and corresponds to design space velocities in the order of $0.2\text{--}1\text{ h}^{-1}$. To complete this procedure, a multi-bed design was developed, thus minimising axial mixing effects. Laboratory data, working with extrudates, indicated superior performance of down-flow over up-flow. This was attributed to the minimisation of forward mixing in the down-flow design, the explanation being that forward mixing would be promoted by the wakes of the rising bubbles in up-flow. This becomes critically important when, as noted above, conversions of >99.99 % are sought. Under these circumstances even minor forward mixing and bypassing can be critical. This design is documented elsewhere [5], but in brief comprised a series of down-flow beds with hydraulic gravity flow between them, controlled by a series of fixed baffles (see Fig. 26.1).

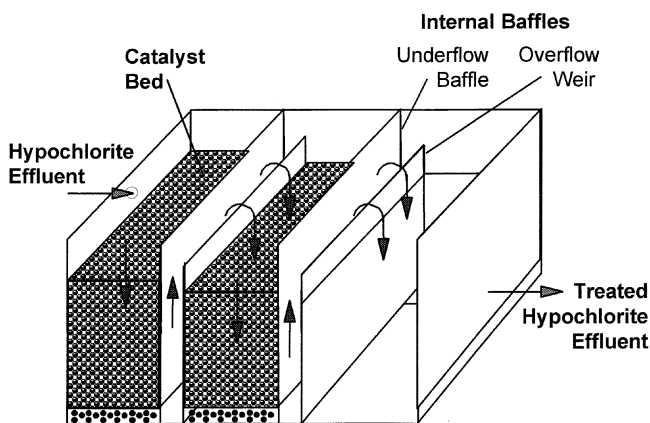


Fig. 26.1 Reactor with multiple down-flow beds for high conversion.

Reactors based on the multi-bed, exclusively down-flow design have been successfully installed and operated at over 20 sites world-wide, all achieving their design exit hypochlorite specification. Units have now been operating for over six years and a catalyst life in excess of three years has been demonstrated. The success of this HYDECATTM (trademark name of the ICI group of companies) technology has recently been recognised by a Queen's Award for Environmental Achievement and the technology has also been granted Millennium Product status by the UK Design Council.

26.5.1 Reaction and reactor modelling

The intrinsic kinetics were described using a Langmuir–Hinschelwood-type expression

$$V \frac{d[\text{NaOCl}]}{dx} = \frac{k_0[\text{NaOCl}]}{1 + k_1[\text{NaOCl}] + k_2[\text{NaOH}]} \quad (26.10)$$

where V is the reactor (or catalyst volume), and $[\cdot]$ is the concentration of the given chemical species. The fitting parameters (k_0, k_1, k_2) are all expressed as an Arrhenius-type function of temperature. Sodium hydroxide acts as an inhibitor for the reaction, due to competitive adsorption on the active sites of the hydroxide and hypochlorite ions. At low hydroxide concentrations the reactions are well-modelled by simple first-order kinetics.

The hydrodynamics were modelled simply, using an average hold-up and slip velocity approach

$$V_{\text{slip}} = \frac{U_G}{\varepsilon\phi} + \frac{U_L}{\varepsilon(1-\phi)} = U_0(1-\phi) \quad (26.11)$$

where V_{slip} is the bubble slip velocity, U_G and U_L are the gas and liquid superficial velocities respectively, ε is the catalyst bed fractional voidage, ϕ is the fractional gas hold-up in the catalyst bed and U_0 is a constant or ‘characteristic’ velocity. The value for V_{slip} was estimated from experimental observations. For design and rating calculation purposes, the calculated gas hold-up was simply treated as a dead volume and the effective catalyst volume for rate calculations proportionately decreased.

This approach is proven for design and prediction of the performance of multiple-bed down-flow reactors. The complication, and a critical difference between this and a bubble column, is that the gas bubbles are formed *in situ*. The gas flux, and thus gas hold-up, will vary over the bed height. For the down-flow beds, a simplified linear gas hold-up profile was inherent in the design models, but with no apparent penalty in design accuracy.

While clearly not strictly correct in terms of the churn of turbulent bubbles and a bimodal size distribution observed in practice, the superficial velocities to be used in commercial units were not significantly different from those used at the pilot-scale process to observe the hydrodynamics. This approach was successful in providing guaranteed performance of installed down-flow reactors.

26.6 Study of alternative design options

Traditionally, processes have used a single destruction technique, and this has historically been the case also for HYDECATTM. Thus, nearly all installed processes treat the waste hypochlorite at the concentration it exits the scrubbing system down to concentrations suitable for discharge (Fig. 26.2). The key aspect in the re-evaluation described herein is to question the practices of firstly ‘single technology’ and secondly ‘end-of-pipe’ treatment: the destruction of the hypochlorite exclusively in the blow-down stream from the scrubber. That is, it is questioned whether installation of a single treatment technique solely to process the effluent at its natural concentration from the scrubber loop is necessarily the best process option. This chapter will consider the two parts of the question paraphrased above sequentially.

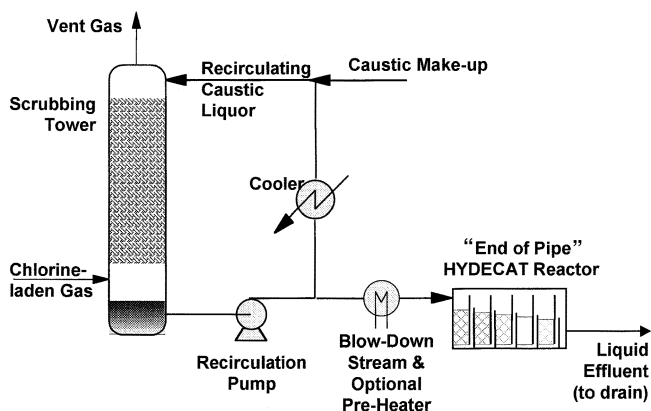


Fig. 26.2 Flow diagram for 'end-of-pipe' treatment.

26.6.1 End-of-pipe process options

If, for instance, destruction is to be installed as an end-of-pipe option, what is the best option? This is a difficult question as the answer depends on the flow rate as well as the actual feed and required exit concentrations. If we consider the alternatives of catalytic decomposition and chemical treatment then the operating cost dependencies are of course very different. For the chemical treatment process the operating cost is the stoichiometric demand of the chemical which is in direct proportionality with the mass rate of hypochlorite to be treated, plus a margin to account for the common practice of over-dosing and plus the operating manpower requirement. For the catalytic process, however, the dominant operating cost comprises the periodic catalyst replacement and negligible supervision of the process that is required. To a first approximation, assuming the known or guaranteed catalyst life, then the operating cost is proportional to the catalyst volume. Thus for comparative purposes:

- operating cost of chemical treatment: $\Gamma_{\text{op(chem)}} \propto Q(C_{\text{in}} - C_{\text{out}})$ (26.11)

- operating cost of catalytic process: $\Gamma_{\text{op(cat)}} \propto Q \ln(C_{\text{in}}/C_{\text{out}})$ (26.12)

where Q is the flow rate of effluent and C_{in} and C_{out} are the reactor feed and exit concentrations, respectively. This fundamental difference in the relationship leads to different trends in the operating cost curves, shown in Figs 26.3 and 26.4 for varying feed and exit concentrations, respectively. It becomes apparent, when considering consumables (catalyst and chemicals) alone that catalysis is better at higher concentrations and the converse at the lowest concentrations; but note that this observation is for consumables cost and excludes manning. It is apparent from this that there exists an optimal design, in terms of consumables cost.

Clearly, when considering chemicals and/or catalyst cost alone there is an economic optimum design that is a hybrid process involving catalytic treatment for the high

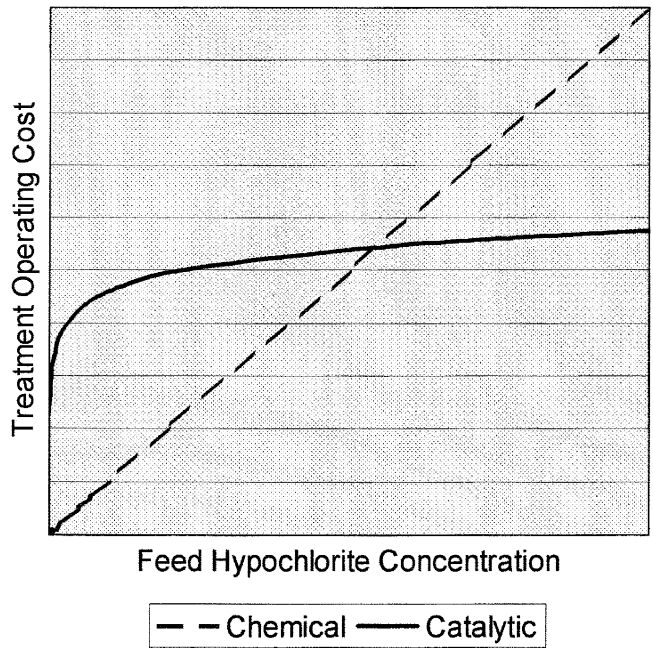


Fig. 26.3 Cost of hypochlorite destruction as a function of inlet concentration.

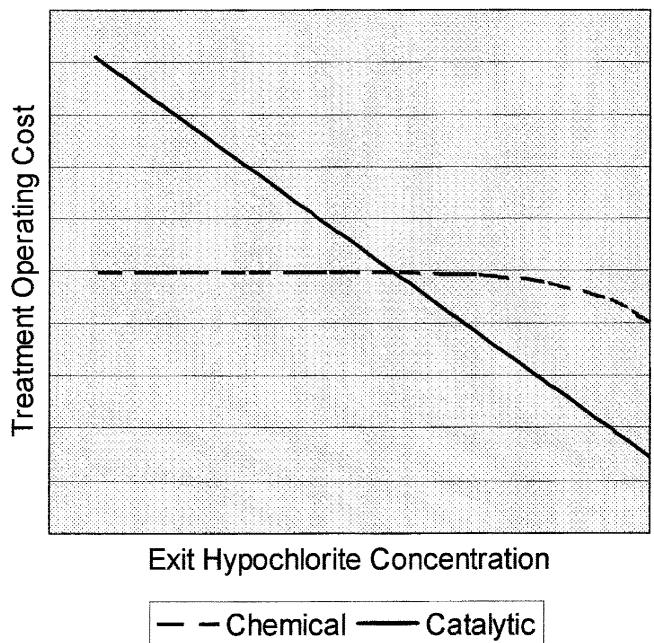


Fig. 26.4 Cost of hypochlorite destruction as a function of exit concentration.

concentrations passing on to chemicals treatment for the low concentrations (Fig. 26.5).

The consumables cost element is shown in Fig. 26.6 where the x -axis is the design hypochlorite concentration at the exit from the catalytic reactor and thus also the feed to the chemical treatment unit. From this it can be seen that at the optimal design the vast majority of the hypochlorite is best decomposed using catalytic means with the chemical treatment simply used to 'mop-up' the low concentrations.

It should be noted that these considerations apply strictly to the consumables element. In the operation of a chemical dosing unit there is the additional fixed cost of manning the operation which, as noted above, is negligible for the catalytic reactor and process.

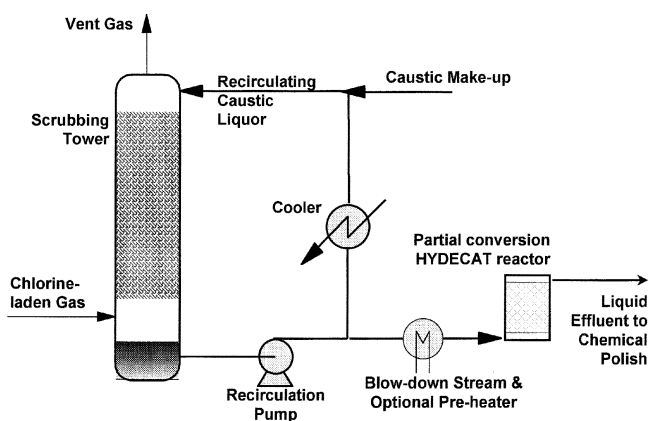


Fig. 26.5 Process flow diagram for hybrid process with partial destruction by catalytic reaction.

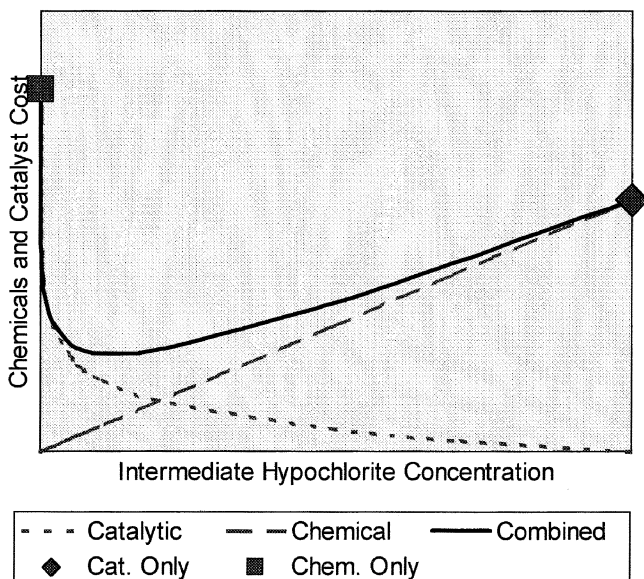


Fig. 26.6 Optimal design of a hybrid treatment process.

When capital costs are also taken into consideration the picture changes again. In the experience of the present authors, it is rarely worthwhile to install a new hybrid unit. The best option will almost invariably be to install a catalytic reactor alone; the marginal cost of completing the low-level decontamination is less than the costs associated with the chemical treatment unit.

An economic benefit can occur through the retrofitting of a catalytic reactor, designed to perform partial destruction of the hypochlorite, into a plant already equipped with a chemical treatment system. The savings in chemicals consumption can more than offset the capital investment associated with the catalytic reactor and purchase of the initial catalyst charge. At high feed concentrations, say above a few weight per cent, the payback time can in fact be less than six months.

At these lower conversions, the previously described multi-bed down-flow reactor may not be the best design. At the higher space velocities it is more expedient to have the liquid in up-flow, and the reduced penalty from axial (particularly) forward mixing means also that the necessary conversion can frequently be achieved in a single catalyst bed. Thus, the reactor design is considerably simplified, with an associated reduction in the capital cost for a given catalyst volume. The development of the design for an up-flow-packed bed reactor for the decomposition of sodium hypochlorite is described elsewhere [6] and will not be considered in detail here.

26.7 Destruction within the scrubber loop

As noted above, batch and semi-batch-based operations result in periodic high loads and subsequent over-design and increased capital cost. By destroying the hypochlorite in situ, within the scrubber recycle loop, the end of cycle concentration can be reduced and the load on the 'end-of-pipe' hypochlorite destruction system lowered allowing an overall cost reduction. The reduced free chlorine concentration also leads to improved process safety, although increased heat removal is required.

Dynamic simulations of a batch-operated scrubber with pump-around will be presented showing the effect of process configuration on destruction demands, where the method of hypochlorite destruction is a fixed-bed catalytic reactor.

Regarding the catalytic reactor, the switch from low space velocity total destruction (end-of-pipe) to a high space velocity partial destruction (in the scrubber loop) has required a change in reactor design concept to that presented previously. The key design consideration changes from avoidance of axial mixing to maximising the rate of gas disengagement. This was addressed through a reactor development programme involving laboratory and pilot-scale testing as well as approximate modelling of the multiphase flow that is described elsewhere [6].

Although the main cost advantage arises in batch systems the same principle can be applied to continuously operated scrubbers. This allows operation at a lower standing hypochlorite concentration in the scrubber and thus leads to improved process safety

through reducing the opportunity for over-chlorination. Process simulation and cost optimisation indicate that this process configuration does in fact allow reduced capital costs. Results from process simulations and cost modelling will be presented.

The process concept is shown in Fig. 26.7 where the recycle loop of the caustic scrubbing liquor passes through a fixed-bed reactor and then through the normal cooler. The blow-down of spent caustic and make-up with fresh caustic can be carried on in the same fashion as without the in-loop hypochlorite decomposition. Consideration of the optimum locations for removal and addition may, however, be slightly different.

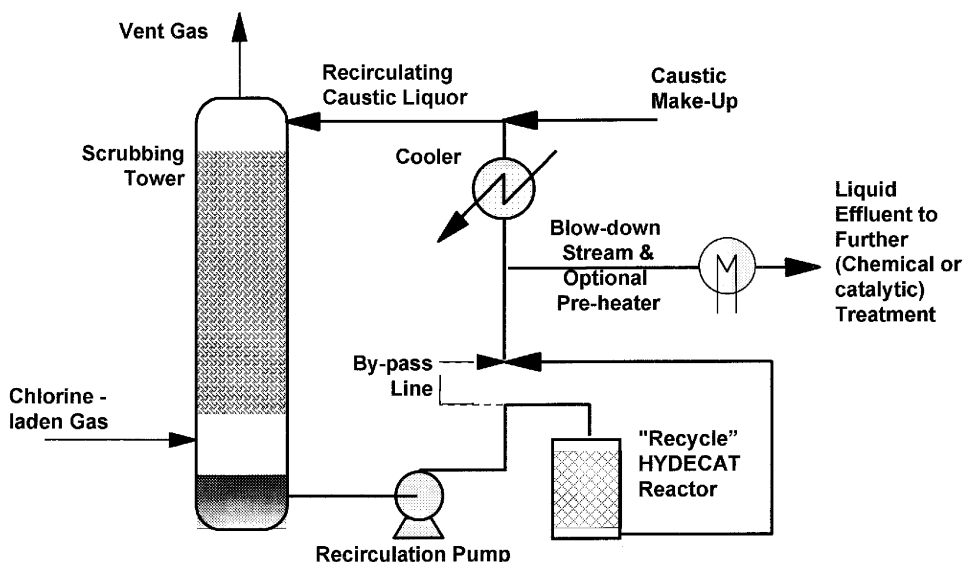


Fig. 26.7 Catalytic hypochlorite decomposition integrated into the scrubbing process.

26.7.1 Batch operation case study

Consider a chlorine scrubbing unit operated semi-batch-wise. That is, a system similar to that shown in Fig. 26.7 is operated batch-wise but, periodically, a portion of the contents of the sump are sent to treatment and the sump refilled with fresh caustic. This mode of operation allows continuous treatment of the chlorine-laden vent stream while allowing batch operation without the need for a dual scrubbing-liquor reservoir.

As an indicator of conditions, the process treats 5 g s^{-1} of chlorine, which for the purposes of the simulation was assumed to be steady arisings, although in practice there was significant variation as a function of time and specific plant operations. There was a recirculation vessel in addition to the column sump and the combined inventory was approximately 5 m^3 , approximately half of which was discharged and replaced at the blow-down and make-up period. The recirculation rate to the scrubber

was $20 \text{ m}^3 \text{ h}^{-1}$. The fresh caustic was 20 wt% and the end-point of the batch (start of blow-down) was set at 5.0 wt%.

A simple model of the batch process was compiled using a commercial spreadsheet program, using finite time elements. A macro was written to obtain convergence of start and end of batch conditions. This model was simple to construct and proved satisfactory in calculating the batch profiles for operation without, and subsequently with, the catalytic reactor on-line. The values obtained for operation without the in-loop catalyst compared well with plant values.

The concentration traces for normal operation are shown in Fig. 26.8 as a function of time through a single batch. The concentrations shown are those in the column sump. From this it is evident that, periodically, approximately 2.5 m^3 of sodium hypochlorite at an average concentration of 13–14 wt% is removed from the scrubber system and requires treatment before discharge. This led to a heavy, and therefore costly, demand for chemicals. Equally, however, traditional ‘end-of-pipe’ design approaches for the catalytic process proved costly because of the envisaged flow rates. In collaboration with a number of potential customers alternative flow-sheet configurations were studied. The above simulation was repeated and converged for the same process but with a catalytic reactor in the recycle loop. For the purposes of the simulation it was assumed that the heat exchange duty had been increased to account for the heat generated by the decomposition exotherm, and as such operation of the scrubber is at the same temperature in both cases. This is a little cooler than is ideal from catalytic reaction-rate considerations, but the view was taken that it was more

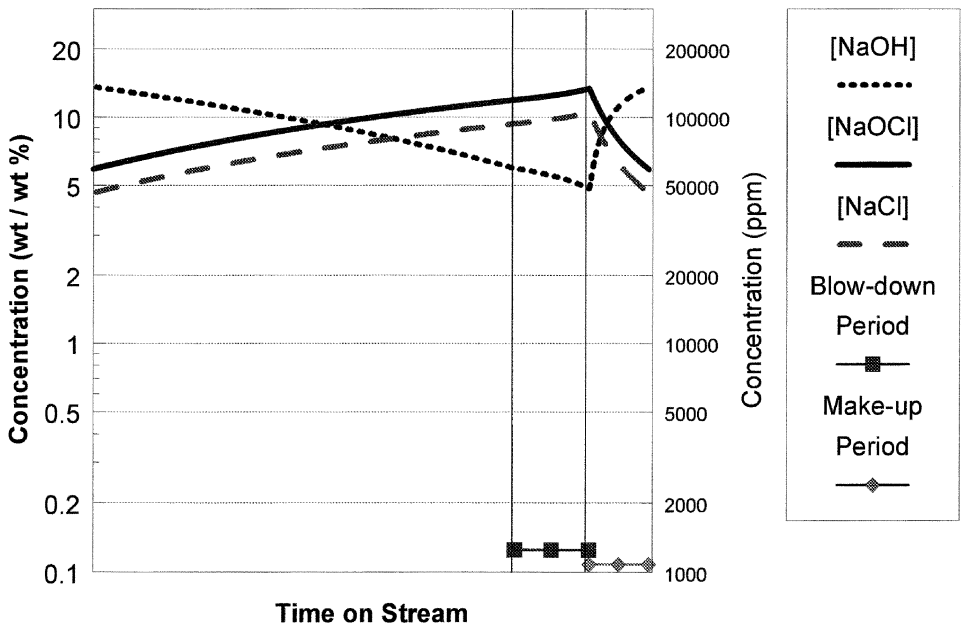


Fig. 26.8 Batch profiles of concentration for operation without in-loop decomposition.

important to maintain the scrubber at its historical operating temperature and assure confidence in the safety of operation of the scrubber and in the chlorine sorption efficiency.

The results are shown in Fig. 26.9 where the sump concentrations are shown in addition to the concentration in the recycle loop exit of the catalytic reactor. Significant differences are observed. Firstly the sump concentration of hypochlorite is significantly lower throughout the batch with the catalyst in operation. Secondly, because the blow-down is taken from downstream of the reactor, the discharged hypochlorite concentration is a further order of magnitude lower. The rise in recirculating hypochlorite concentration during blow-down observed in Fig. 26.9 is because of a slight flow-sheet difference from that shown in Fig. 26.7. The recirculation during this period by-passed the reactor allowing maximum space time for the blow-down stream in the reactor and therefore minimisation of the discharge hypochlorite concentration sent on to, in this case, a chemical treatment unit. Preliminary calculations showed that the savings in consumables offset the investment in plant modifications and installation of the single-bed, up-flow reactor to the extent that the payback period was less than six months.

Table 26.1 shows the effects of the two main design variables. Specifically, the results of the batch simulations for the same system as described above are given for different in-loop reactor (catalyst) volumes, recirculation rates. As would be expected increasing the catalyst volume decreases the hypochlorite concentration at all points and times through the process. Increasing the recirculation rate also appears to have a

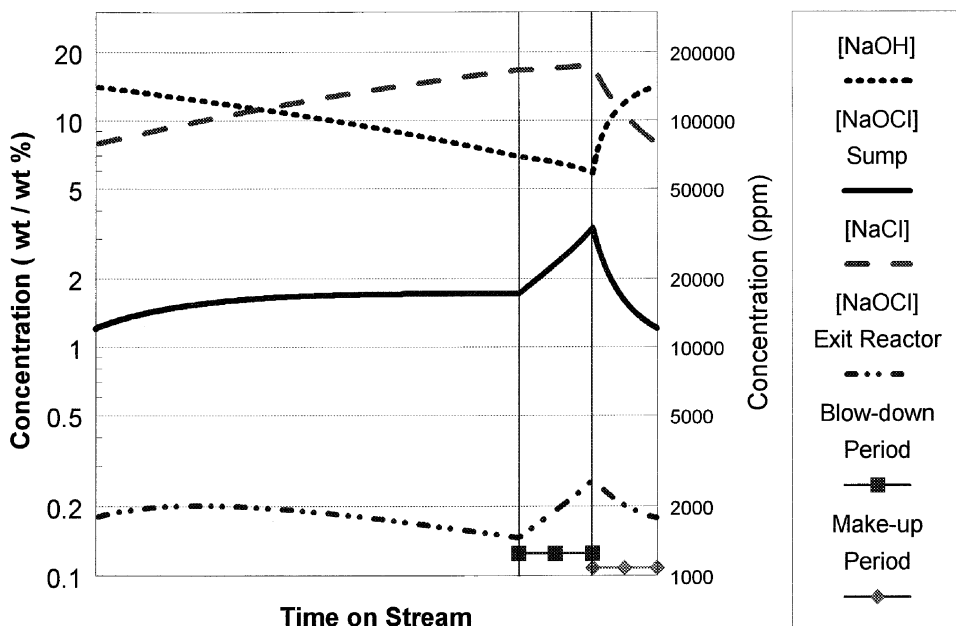


Fig. 26.9 Batch concentration profiles with integrated hypochlorite decomposition.

Table 26.1 Effect of process parameters on hypochlorite concentration.

Case number	0	1	2	3
Case definition				
Catalyst volume	0	V	2V	2V
Reactor feed rate	0	Q	Q	2Q
Case results				
Average blow-down NaOCl	10.00	0.90	0.15	0.30
Maximum recirculating NaOCl	10.00	3.06	2.54	1.49
Average recirculating NaOCl	7.01	1.79	1.27	0.82

beneficial effect because the average concentration in the reactor is increased and thus the overall rate of decomposition decreased. This does not of course take into account the operation of the scrubber and the consequential increase in gas-phase pressure drop, which may not be allowable.

26.7.2 Continuous operation studies

The advantages of a decomposition reactor integrated into the scrubbing liquor recycle loop are evident for batch and semi-batch operations and arise from the advantages of treating the hypochlorite on a more continuous basis and thus reducing the equipment size and associated costs. What is possibly more surprising is that in some circumstances there are also advantages for continuous operation. This would not necessarily be expected as, firstly, the average concentration at which the stream is treated becomes lower, and thus the rate slower, and secondly, because the exotherm of reaction is dissipated rather than effectively heating the reactor, the reactor temperature is thus reduced, again slowing the rate of reaction. The counter-effect, however, is that now a portion of the catalyst is housed in a relatively lower cost single-bed reactor and thus the overall capital cost may in fact be decreased. One clear benefit is that, unless the column is being run to manufacture saleable hypochlorite, then the in-loop catalysis reduces the standing hypochlorite concentration and thus improves safety.

The most significant economic benefit is where the natural hypochlorite blow-down concentration is greater than 8–10 wt%. In an end-of-pipe reactor, if the concentration is above approximately 10 wt% then the decomposition reaction leads to salt precipitation and a reversible loss of activity. The salting out is in fact caused by the drying out of the catalyst surface owing to the evaporation of water into the evolved gas. In process design, and in actual operation, it is therefore necessary to dilute any such stream prior to feeding to the reactor. This has the knock-on effect that it is necessary to dilute the reactor feed and accordingly the reactor is proportionately larger. By treating the solution within the scrubbing loop, the concentration is suppressed at all points and thus the need to dilute obviated.

In fact, the above design scenario requires very low overall pass conversions to achieve significant reductions in the standing hypochlorite concentrations. It is

therefore practical to pass only a portion of the pump-around through the catalyst, or indeed provide an alternative pump-around explicitly for the reactor. Consider a continuously operated system, as was depicted in Figs 26.2 and 26.7, for the addition of an integrated reactor. In a system where the chlorine rate is 360 kg h^{-1} (steady arisings) and the aqueous recirculation rate around the scrubber is $180 \text{ tonnes h}^{-1}$, the make-up caustic soda, at 20 wt%, is added at a rate of $1.8 \text{ tonnes h}^{-1}$. Table 26.2 shows the effect of some of the process variables on the recirculating hypochlorite concentration.

Table 26.2 Reduction in hypochlorite concentration for a continuous system.

Case number	Base	1	2	3	4	5
Catalyst volume (relative)	0	0.016	0.19	0.36	1	1
Proportion of pump-around fed to catalytic reactor (%)	n.a.	25	10	25	10	50
Hypochlorite concentration in the recirculation vessel (wt%)	12.25	3.23	3.23	1.69	1.69	0.6

These data show that even by pumping a small portion of the recirculation through the reactor, a major reduction in the hypochlorite concentration is achieved. It should also be noted that this does not necessarily require large catalyst volumes: the actual catalyst volume for both cases 1 and 2 is less than 1 m^3 .

Economic analysis of designs at lower natural hypochlorite strengths equally show potential investment benefits. They are, however, much less significant than the batch and high concentration cases described above. While an economic case can be made for retrofitting an in-loop reactor to a system that already has an end-of-pipe treatment system based on payback, it is not always clear that this is a better option than an end-of-pipe hybrid system as described earlier in the chapter. For a particular system the optimum solution is often as much a function of the required expenditure on the heat exchangers as it is the relative cost of the reactor options.

26.8 Conclusions

Traditionally, waste hypochlorite streams have been treated at the concentration that they naturally exit the vent scrubber, using a single-treatment technology, where the technique is typically chemical dosing or catalytic. This study has shown that for many plants this may not be the ideal solution. Where a completely new installation is required then a single-treatment technology is probably the optimal design, and for feed concentrations at the 1000 ppm level and above, the best approach is probably catalysis. For retrofits into an existing plant, however, alternative approaches should be considered.

In the case where an existing chemical treatment unit is already in place, then the

preferred strategy may involve a hybrid process. The initial treatment, at high concentrations is catalytic and the clean-up to very low levels can continue to be performed with the existing chemical treatment system. The overall optimisation is complex and includes consideration of the fixed-cost manning requirements of the chemical treatment. This design results in lower conversions and higher space velocities than the more traditional end-of-pipe solution and as a result a simpler, lower cost reactor may be used. Short payback times on the incremental investment through savings in chemical costs can be demonstrated.

In batch processing, high treatment costs arise because the treatment unit has to cope with the periodic high loads and this results in significant over-design. An alternative approach is proposed where, through use of a catalytic hypochlorite decomposition reactor in the pump-around loop the hypochlorite may be decomposed as it forms, reducing the end-of-batch concentration and significantly reducing the cost of chemical treatment of the spent caustic from a given batch. As with the partial conversion approach above, at pass conversions of only 90% and the high space velocities involved, a simple single-bed up-flow reactor design is preferred.

For continuous processes the catalytic reactor, or a hybrid process if satisfactory chemical dosing equipment is already installed, appear to be a near-optimum solution still for many installations. At moderate hypochlorite concentrations, economic benefit does accrue from using the catalyst in-loop rather than end-of-pipe, but these benefits may be offset by any required investment in heat-exchange capability. At concentrations above 10 wt% the integration of decomposition into the scrubbing process is beneficial to the overall cost base of hypochlorite treatment.

This chapter has therefore shown that cost minimisation of the treatment of hypochlorite effluent streams is achieved only through consideration of a wide range of process alternatives. The optimal solution for a given plant is dependent on a number of aspects, which include not only the rate and concentration of the stream as well as its required exit concentration, but also the configuration and operational mode of the caustic scrubber and any existing treatment system.

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